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THE PRINCIPLES

OF

INORGANIC CHEMISTRY

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OF

INORGANIC CHEMISTRY

BY

WILHELM OSTWALD

TRANSLATED WITH THE AUTHOR'S SANCTION

BY

ALEXANDER FINDLAY

M.A., B.Sc., Ph.D.

WITH 122 *FIGURES IN THE TEXT*

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DEDICATED

TO MY DEAR WIFE

Helene

IN GRATITUDE FOR LOYAL HELP

TRANSLATOR'S PREFACE

In presenting the accompanying translation of the *Grundlinien der anorganischen Chemie* to English-speaking students, the translator hopes to be thereby contributing somewhat to a more wide-spread knowledge of the application of the more recent developments of General Chemistry, and consequently to a juster appreciation of their importance in the study of the other branches of the science.

In the present translation the mistakes which had crept into the German edition have been, as far as possible, corrected, and otherwise various minor changes have been made. As, however, these have all been made either at the author's suggestion or with his approval, special attention need not be drawn to them.

One change, however, relating to the nomenclature of the ions, calls for special mention. The terminology adopted in this translation, with the approval of the author, is that proposed by Professor James Walker, F.R.S. (*Chemical News*, 1901, **84**, 162). I would express my thanks to Professor Walker for his kindness in placing this nomenclature before me in time for its incorporation in the present translation.

The proof-sheets have all passed through the hands of the author, and I would here express my indebtedness to him for suggestions made while the book was passing through the press. My best thanks are also due to Messrs. R. S. Hutton, M.Sc., and Sydney A. Kay, B.Sc., for their invaluable assistance in reading the proof-sheets.

A. F.

University College,
London, *January* 1902.

PREFACE

The first sketch of the present work dates back double the time designated by Horace as necessary for the maturing of a literary work, and some of the attempts to overcome the difficulties which were then met with have occupied me during the whole period of my activity as a teacher. The recognition that such a task is, by its nature, unlimited, and that it is possible to *round it off* but not to *bring it to a conclusion*, finally brought the resolution to maturity to give publicity to the accompanying attempt.

The task which hereby presented itself was to so incorporate the new notions and theories of scientific chemistry in the course of instruction that the student would, from the beginning, be made acquainted with the improved views instead of having first to learn the older, untenable notions, only to find out later that these must be abandoned. It was therefore necessary to considerably alter the fundamental form which is at present found, with slight modification, in the present text-books. I have endeavoured to do this only to such an extent as appeared to be demanded by the object in view, and have retained as much as was possible of the approved forms. If in this respect I have been too radical in my procedure for the feelings of some of my colleagues, it should be remembered that new cloth in old garments will not suffice here. On the contrary, a connected whole can be produced only when it is formed in its entirety by *one* mind and executed according to *one* plan.

I have retained, in the first place, the naturo-historical arrangement of the subject matter. One could, perhaps, even now venture the experiment of constructing chemistry from the commencement as a rational science on the basis of a few general principles, and introducing the description of the various substances only in illustration of these general laws. I have been deterred from this by the exigencies of the historical connection, and by the recognition of the fact that the diversity of substances is too great and a knowledge of each of them too important to allow of such a method of treatment being made use of for instruction at the present time. The course I have pursued, therefore, is to insert the general laws in the traditional frame of the naturo-historical arrangement according to elements and their compounds, at those points where cause and opportunity for it presented themselves. The task to be accomplished here has some resemblance to an artistic problem; for the insertion of the general laws could not be left to chance occasions, but these laws themselves had to follow a systematic arrangement which would ensure their comprehension and the recognition of their mutual connection. Accordingly, I cannot regard the solution attempted by me as the only possible one, and can imagine numerous other ways of attaining the end. It appeared to me, however, to be worth while to endeavour to prove that such a course of instruction is possible at all.

A text-book which pursues reformatory plans of the above nature appeals naturally to two kinds of readers, the teacher and the student, and has therefore a double task to perform, which increases the labour not a little. In this connection I have always, in cases of doubt, first had regard to the requirements of the student, and have thereby been led to a certain fulness of treatment which would not have been necessary had I written exclusively for the teacher. If the latter has to take much that is "self-evident" along with the rest, he has, on the other hand, the convenience of finding the subject-matter already formed into shape, and only requires to modify it according to his personal views, without himself having to carry out the remoulding of the material for his pupils.

With regard to the student, I have felt myself pledged to the carrying out of the chief thought, viz.,—to offer him a really systematically arranged subject, strictly developed in such a way that for a comprehension of the new facts only a knowledge of that which has preceded is assumed, not of that which follows. To render the first study more easy, the discussions which in a first reading may be omitted, either because of their being more foreign to the subject in hand or because of especial difficulties, are marked with an asterisk. In all cases I have made it a rule to introduce general discussions only when some readily intelligible facts furnished an example to which these considerations were to be applied. I have therefore not hesitated to return repeatedly to the same question whenever it appeared to me that its complete discussion at the point where it was first introduced would lead too far afield. The beginner, especially, I hope to have more than compensated for the loss of systematic strictness which such a method makes necessary, by the assurance of a greater familiarity with the subject.

For the carrying out of the rational construction of the chemical system, a method has proved suitable which, as has meanwhile appeared, was always applied by the recently deceased great master of chemical investigation and teaching, Robert Bunsen. It consists in giving a short summary of the chemical relations which are familiar to every one from his daily life, after the fundamental conceptions of chemistry have been established, but before the regular description of the substances and their transformations. This summary appropriately follows on the introduction of the conception of *chemical elements*; not only does that conception thereby receive ample illustration, but the further advantage is obtained that where, as so often occurs, the necessity arises of mentioning substances which are treated only at a later point of the course, reference can be made to what has there been said.

I have exercised particular care in the development of the *conception of ions.* Sufficient attention is perhaps not paid to the possibility, the necessity even, of introducing this conception as a purely chemical and not as an electrical one. Even although, historically, it arose as the latter, its importance in chemistry depends essentially on its giving expression to the chemical fact of the *individual reactions of the components of salts*, and it is in this sense that I have developed it. The facts of electrolysis and Faraday's law serve then only to widen and to deepen the conception obtained by a chemical method. I believe also that this is the way in which these views can be introduced even at a very early stage of chemical instruction, without making too great demands on the pupil.

In this connection I cannot refrain from expressing my conviction that, compared with formerly, the demands made on the intellectual co-operation of the student of chemistry must be increased. In proportion as chemistry develops from the condition of a descriptive to that of a rational science, it makes greater claims on the powers of thought and abstraction of its disciples. In this respect it approaches more and more to physics. Since, indeed, it is chiefly the same students who are at the same time learning chemistry and physics, the intellectual activity with which the student of physics is accredited may also be claimed for the student of chemistry. I cannot conceal the fact that I have always been greatly grieved by the conscious descent to a lower intellectual stage which is so often found in elementary chemical text-books as compared with the text-books of physics or of mathematics designed for the same period of study. This circumstance is certainly to a great extent the cause of the idea which so readily arises among the younger physicists that chemistry is a science of a lower rank.

If the present-day chemistry, therefore, makes greater demands on the power of rational thinking, it also renders the purely memory work of mastering the subject considerably more easy for the student. The growth of the scientific interpretation and elucidation of the separate facts of chemistry facilitates in the highest degree the impression of them on the mind and their application, and at the same time affords an incomparably greater intellectual enjoyment than the study of the older, essentially descriptive chemistry could offer. From the experience gained from laboratory teaching during a number of years, I believe I may assert that it is just for those students who are endowed with some tendency towards independent thinking that the study of chemistry becomes both more easy and more living through its presentation in the modern spirit.

A few words ought also to be said regarding the fact that the intention of the present book is to be a text-book of *pure* chemistry. Regard has been paid to the related sciences and arts only in so far as *chemical* questions play a part in them. This holds in the first place for chemical technology, and also for medicine, agriculture, political economy, etc. The need of rendering more palatable the "in itself dry" material of chemistry by the addition of such matter has not been experienced by me, nor can I recognise its existence. The subject-matter of chemistry is dry only when it is limited to an enumeration of properties and to a collection of preparative receipts. So soon as it is treated in a truly *scientific* manner, each chemical compound becomes the centre of so much general and therefore interesting discussion that embarrassment is felt not on account of the lack but on account of the abundance of relationships. In proportion as any branch of study becomes more scientific, the necessity arises of restricting it to its own sphere.

Of course we do not here speak against the acquirement of a solid knowledge of the related sciences by the future chemist. On the contrary. But such knowledge will be all the more solid the more it is acquired by special study directed to that object; for the indications, necessarily scanty and incomplete, to which a text-book of chemistry must limit itself, rather give rise to the danger that the student thinks he knows things of which he has on some occasion heard such indications, and considers a closer study of them to be unnecessary.

Much might still be said to explain and justify the method of treatment wherein the present book differs from others written for the same purpose. The finding out and the criticism of these details, however, ought, I think, to be left to the expert teacher of chemistry. In the interest of the *student*, I have in all cases avoided a polemical discussion of opposing opinions; and although I am prepared to grant the possibility and probability of mistakes in the views which I have here given as appearing to me to be the most appropriate, I nevertheless believe that I may assert that these views are the outcome of careful consideration. The first three chapters, for example, were rewritten four and, in part, five times before they assumed the form which they now have. I would therefore beg the reader to believe, in cases where doubt may exist, that there was some special reason for the particular position adopted. This does not exclude but rather involves my readiness, in any given case, to honour any opposing views.

May this book, then, which, in a certain sense, forms the coping-stone of a long course of active work pursued with affection towards the general introduction and extension of the new foundations of chemistry laid by Horstmann, Willard Gibbs, van't Hoff, and Arrhenius, achieve the good hoped for, and help to enlist and train new troops for the victorious march of our splendid science.

I cannot conclude these introductory remarks without remembering in gratitude the excellent assistance afforded me by Messrs. Böttger, Bodenstein, Brauer, Luther, and Wagner, in that they read the proof-sheets and gave me much good advice both as regards the form of treatment and the subject-matter. My special thanks are further due to Mr. Brauer for the preparation of the figures,—over one hundred in number,—which were specially drawn for this book. It will be easily seen that they are not diagrammatic, but sketched from apparatus actually put together; they thereby form a considerable part of the didactic portion of the book relating to the performance of experiments.

W. OSTWALD.

LEIPZIG, 31*st July* 1900.

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CHAPTER I

GENERAL PRINCIPLES

Chemical Phenomena.—The objects and processes which make up the outer world of man, form the material of Natural Science. Although, in reality, there is only *one* Natural Science, extending over the whole range just indicated, still the necessity of facilitating the survey of the whole extent of our knowledge had led, even at an early period, to the formation of subdivisions, in which were grouped together phenomena more closely related to one another, *i.e.* similar phenomena. Such a subdivision is formed by Chemistry.

The exact definition of the subject-matter of chemistry and of the boundary between it and the other branches of science related to it, cannot be given at this point, since for this purpose there is necessary a knowledge of facts which have first to be given in this work. Still, it will simplify matters for the beginner to give him a token by which most of the chemical phenomena can be recognised, and which will therefore afford him guidance as to the direction in which he has to give his attention.

In the world outside of us, we recognise regions of space, marked off and distinguished from what surrounds them, and these distinguishable things are called *bodies*. If we consider some definite body, we often notice that it undergoes some change, *i.e.* its relations to the instruments of sense by means of which we perceive it, and to its environment, are changed. Such changes can be divided into two large, although not sharply defined, groups. *Either they affect only one or some few relations and properties of the body considered, or they are of a more radical nature, such that the body under consideration disappears and its place is taken by other bodies having other properties.*

Phenomena of the former kind belong to *Physics;* those of the latter, to *Chemistry.*

Take, for example, some definite body, such as a piece of sulphur. If we push it, it changes its place; it rolls over the table. None of its other properties, however, undergo change; it retains its yellow colour, its form, its weight, etc. Movement is therefore a *physical* phenomenon.

We can place the piece of sulphur in hot water and it acquires thereby the property of producing the sensation of warmth when placed on the skin. No other change can be perceived. If we rub it with a cloth, it acquires the property of attracting light objects, such as scraps of paper; it has become electrified. Here again, no other change in its properties can be recognised. These phenomena are, therefore, also to be assigned to *physics*.

We now bring the piece of sulphur in contact with a flame. It takes fire and begins to burn with a blue flame. The smell of burning sulphur, also, becomes noticeable, and if the burning lasts some time, the sulphur disappears; it is burnt. In this process, not only do particular properties of the sulphur undergo change, but the sulphur disappears altogether, so that we can no longer see it at all. From the smell which arises at the same time, and which was not there before, we can conclude that something else has been produced from it. In this case, therefore, the sulphur has undergone a *chemical* process.

We recognise such chemical processes everywhere around us. The burning of petroleum and stearin in our lamps and candles, of coal in our fires, the transformation of food-substances in the animal organism, the processes connected with the germination and growth of plants, the rusting of iron, the turning sour of milk, the putrefaction of dead animal and vegetable matter and innumerable other phenomena of a like kind, are identified as *chemical* through the disappearance of existing bodies and the appearance of new ones possessing other properties. To establish the laws of all these phenomena is the task of the science of chemistry.

Experience.—In describing the simple phenomena with which we have just been occupied, we have employed various conceptions and ideas of which we daily make use and which are therefore familiar to us. For scientific purposes, however, we dare not rest satisfied with the somewhat indefinite and arbitrary notions which we attach to such words in ordinary life; their full purport must be examined and their meaning established with definiteness.

That which enters directly into the consciousness of a particular individual, is the changing conditions of his mind. We soon distinguish between the *inner* and the *outer* experiences; the former are dependent on our will, the latter are not, or are so only indirectly. On account of this independence, we assume that such experiences have their cause in something that is different from our person, and the totality of these experiences we call the outer world.

All our experiences form a series of diverse states or processes differing among themselves. An event is never repeated in exactly the same way as it had once occurred.

Our relation to life would, therefore, be that of a wanderer in the darkness of an unknown and trackless region, if it were not that there are events which repeat themselves, not in their entirety, it is true, but still to a large extent. When we have experienced a number of such occurrences, we are in a position to foresee the probable further course of one of them when it recurs. If it is an event which influences our condition in some particular way, we are able to act so as to gain the greatest advantage, or suffer the least harm, from it.

The recognition of such events as in large measure repeat themselves, is called *experience*. It consists, therefore, on the one hand, in the recognition of the circumstances under which definite events occur, and, on the other hand, in our knowledge of the *course* of the events or of the sequence of their parts.

Conceptions and Laws of Nature.—Not science only, but all mental life whatever, begins with the collecting of such similarities and the distinguishing of them from others. Even the brute does this when it seeks shelter in the thicket from rain or from a pursuer, because such action had before proved successful in similar circumstances. The most general relations of this kind are contained in language. Every noun, like "dog" or "stone," signifies that we are dealing with a large series of concordant experiences which present definite and always recurring similarities. For this reason the word sulphur signifies not, let us say, some one definite impression which I have once had at some particular time, but it is the summing up of repeated impressions in which can be recognised a group of different characteristics which always occur together. The sum total of the concordant characteristics—*those which are discordant being excluded*—is then gathered together in one such name.

Thus in the case of the word sulphur, I think of a yellow, solid substance, which can be set on fire, which becomes liquid at a not very high temperature, which sinks, without dissolving, in water, and becomes electrified on being rubbed. I do not think of sulphur as having a definite shape or size, but rather I denote by the name a piece of any size in which I recognise the properties mentioned. In the formation, therefore, of the name sulphur, there has by no means been taken into account the sum total of all properties of some definite single piece, existent or imaginary. On the contrary, no attention has been paid to the size, form, and origin of the single bodies to which I give the name of sulphur, but account has been taken only of such properties as are found in all pieces, independent of these differences.

Such an exclusion of differences in phenomena which in other respects are similar, is called *abstracting*, and the result of the abstraction, which in the more simple cases is condensed into one name, is termed a *conception*.

As is evident, one and the same phenomenon can be classed under different conceptions, according to the similarities of which we take account. The range of a conception, or the number of single phenomena which can be included under it, can be so much the greater, the fewer the points of agreement which are considered. At the one extreme are the single names which mark individuals, *i.e.* objects which are to be characterised as only of solitary occurrence. In this case we have very great variety, and generalisation consists only in the object always preserving essentially the same properties for a certain time—its period of existence.

At the other extreme are the general conceptions, such as "thing" or "object," in which emphasis is laid on no other property than on that, that it can be distinguished from other things.

Now, the most important work of the sciences consists in the formation of suitable conceptions. A suitable conception is, however, one under which is embraced as large a number as possible of single phenomena in such a manner as to contain the largest possible number of definite statements regarding each. The content of such statements is given by the *Laws of Nature.*

Time and Space.—One of the first things we experience, is the change of day and night, and the unbroken repetition of this change of light and darkness in our surroundings, has therefore led to a fundamental conception, that of *time.* Since this change is quite independent of our will, we employ it as an *objective* measure of the events of our life, and refer these to the marks or signs which the change of day and night affords us.

For many occurrences this measure is too large. It is therefore divided into parts. The $\frac{1}{24}$th part of the day-and-night period, called the *hour*, is used as the unit in daily life. For scientific purposes, the $\frac{1}{3600}$th part of an hour, or the $\frac{1}{86400}$th part of the whole period, serves as the unit, and is called the *second.*

Experience also teaches us that innumerable differences in things can exist side by side *at the same time.* This diversity is condensed in the conception of *space*, in which are summed up all generalities and similarities by means of which we can arrange and review co-existent things.

The diversity, which we call *space*, is a threefold one and shows itself in the three dimensions length, breadth, and height. Spatial measurements are carried out either in one dimension (distance or length), or in two dimensions (areas), or in three (space or volume).

The unit of length is the length of a platinum rod preserved in Paris. This is approximately equal to the $\frac{1}{40000000}$th part of the earth's meridian, and was originally intended to be exactly equal to this. Since two rods of this length, however, can be compared with one another with much greater accuracy than the ratio of one of them to the earth's meridian can be determined, that relation has been, very wisely, discarded, and a considerable number of similar rods have been made and compared exactly with the standard one.

These rods are kept at different places, so that should one or other of them by some mischance be destroyed, the unit itself would still not be lost.

This unit is called a *metre.* It is equal to rather more than half the height of a man of average stature. For scientific purposes, the metre is divided into 100 parts, called the *centimetre*, which in writing is abbreviated to cm. Other divisions into decimetre and millimetre, of which 10 and 1000 respectively, are contained in a metre, are better not to be used in science. When the magnitudes which have to be expressed are much greater or much smaller than a centimetre, they are written in the form $m \times 10^n$ cm. The indices most used are $+5$ and -4. The length 100,000 cm. or 10^5 cm., is called a kilometre; a German mile is therefore nearly equal to 7×10^5 cm.[1] The length 10^{-4} cm. is called a micron; it is one-thousandth of a millimetre, and is at the limit of the microscopically visible. It is also denoted by the Greek letter μ.

The measures of area and volume are derived from the measures of length, by taking as the unit of area and volume a square and a cube respectively, the length of whose side or edge is 1 cm. The former unit is called a square centimetre, abbreviated sq. cm., the latter, a cubic centimetre, cc. These are the only units employed for the purposes of pure science. In daily life and also in science, the litre, abbreviated lit., which contains 1000 cc., and which is equal to the cubic content of a cube whose edge is 10 cm., is often used as the unit of volume.[2]

Bodies and Substances.—In the outer world objects can be easily recognised having a definite spatial limit or form and distinguished by their properties from what surrounds them. Such objects are called *bodies.* Every body is characterised by the properties by means of which it can be distinguished from what surrounds it.

If we imagine a large number of bodies placed side by side and compared with one another, we can correlate them in various ways. We can consider their size and form, and arrange them according to these spatial properties, or we may neglect these and consider only the other properties.

If we leave size and form out of account and arrange the bodies in such a manner that those which agree in their other properties are placed in the same group, then the bodies are called *substances.* The files, the knife, the borer, and the various objects on the tool-board, are so many different bodies. If, however, we leave the form of these out of account and consider them with reference to their other properties which are independent of the form, we shall call them the same, for they all consist of the same hard, heavy, and tough material called steel. Steel is, therefore, the *substance* of which the above-named *bodies* consist.

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[1] An English mile is nearly 160,933 cm., or rather less than $1{\cdot}61 \times 10^5$ cm.—Tr.

[2] This method of deriving the measures of area and volume with the help of the square and the cube, is by no means necessary, nor is it the only one. For example, one could use as units a triangle and a tetrahedron of 1 cm. side, a circle and a sphere of 1 cm. radius or of 1 cm. diameter. The choice of the square and the cube is, however, probably the most suitable, since it allows of the easiest calculation of areas and volumes from measurements of linear magnitudes.

In the same way, every one will call the yellow, pulverisable lumps which burn with a pale blue flame, sulphur, no matter whether they are large or small, regular or irregular in form. Sulphur is the name of a substance.

The fact, now, that language possesses a fairly large number of names for different substances, is the expression of a general experience or of a law of nature. Just as in the case of animals and plants, so also *the different inanimate bodies can be separated into definite "species,"* each of which embraces a large number of individuals or single substances with concordant properties. As is known, the number of species in the case of animals and plants, although, certainly, very large, is still incomparably smaller than the number of the individuals. Likewise, the number of substances which differ in their properties although large, is incomparably smaller than that of the single bodies.

This fact can also be expressed by saying that in the bodies there do not occur all imaginable collocations of properties, but only certain definite ones. Every such collocation of properties which does really occur, characterises a definite substance, and the fact that the bodies which occur in nature can be arranged in such groups or "substance-species," is the statement of an important law of nature, *the fundamental law of chemistry*. It is the object of chemistry as a science, to know the properties of substances and the relations which exist between them.

Properties.—What we have termed the properties of substances, can be very varied in kind. Since in the conception of a substance we have left its arbitrary amount and its form out of account, these cannot be regarded as properties of the substance; they are properties which belong to a definite *body*, but not to a *substance*.[1]

On the other hand, properties which belong to a substance are colour, density, power of refracting light, electrical conductivity, and many others. These properties occur in a particular substance always in a definite manner, and to a definite extent. In future they shall be called shortly, properties of the substance.

Besides these, there are other peculiarities which can appear in a body consisting of the substance considered, such as, temperature, electrical charge, pressure, illumination, etc. These we shall call, not its properties but its *conditions*. These differ from the true properties in the fact that they can be imparted to the body or altered at will, without the substance passing into another, whereas the *properties* are always present when the substance is present.

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[1] As the result of an indefiniteness in the use of language which, it is to be regretted, is very wide-spread, one often finds in text-books and memoirs that the two conceptions of body and substance are not kept rigidly separate, but are mixed up in such a way that the word body is often used where substance is intended. Descriptions such as "Sulphur is a yellow, brittle *body*," instead of *substance*, occur very frequently. In this book, we shall always draw a sharp distinction between the two ideas, and it is desirable that the general scientific usage should, in this respect, also assume a more definite form.

The optical properties of a substance, *i.e.* its *colour*, and the manner in which it reflects light, or its *lustre*, are open to direct observation. That a piece of sulphur is yellow, and that the light is reflected to a fair extent from its surface, can be seen at the first glance.

I can learn, however, that the density of sulphur is greater than that of water, only when I place the piece of sulphur in water and note whether it floats or sinks; since it does the latter, I conclude that sulphur is denser than water. In what ratio, however, it is denser, can be learned only by making a quantitative experiment.

So it is also with the other properties of sulphur; to determine them, an experiment must be made. That is to say, we bring the substance into relations which are different from the ordinary, and note its behaviour under these new conditions. In this way we learn that sulphur is a non-conductor of electricity, when we touch a charged electroscope with a piece of sulphur, and find that the gold leaves do not fall together, or when we connect a galvanic cell with an electric bell, and find that the bell does not ring when we insert a piece of sulphur in the circuit. Further, by heating a piece of sulphur in a glass tube, we learn that it melts or passes into the liquid state at a not very high temperature.

The last mentioned experiment, the melting of sulphur, represents a transition to a group of other properties which are characterised by the fact that the nature of the substance itself undergoes change, which it did not do in the former experiments.

The combustibility, likewise, of sulphur when heated in the air, is such a property. Further, if we mix some sulphur with iron powder and heat the mixture in a test-tube, a thin-walled glass tube closed at one end, it suddenly becomes incandescent, and when cold, both the sulphur and the iron are seen to have disappeared, and in their place a black substance has been produced with quite different properties.

Processes in which certain substances disappear and other ones are produced, have already been designated as *chemical*, in contradistinction to the *physical* or those in which the substances maintain their existence. We shall, therefore, divide the properties of a given substance into physical and chemical; the former being those we observe when the substance remains unchanged, the latter being seen when the substances are converted into others.

* The question is often raised, whether processes such as fusion, when the temperature is raised, or solution in a solvent, are to be

regarded as chemical or as physical. Disagreement, however, on this question is without point, since nothing of an essential nature depends on the decision; for this, evidently, is of consequence only with regard to the arbitrary plan of treatment. If we retain the definition already given, we shall recognise that sulphur with its properties certainly disappears when it is made to assume the liquid state, by heating or by treatment with a solvent. It therefore undergoes a chemical change. Many, however, designate such changes as physical, since it is easy to recover the sulphur in the solid form with all its properties, by lowering the temperature or by evaporating off the solvent. But a substance which has undergone chemical change can, in general, also be again obtained from the new substances produced, although more complicated methods are often necessary. It will, therefore, on the whole, be better to class these changes along with the chemical.

Homogeneous Substances and Mixtures.—Whereas in everyday life, for the purpose of characterising a substance, we make use of those properties which appeal to our senses, and which allow only of making rough distinctions, it is the task of chemistry to ascertain with all possible exactness all the properties which can be employed for the characterisation of a substance in the sense in which we have defined it. This is possible, however, only when every part of the substance has exactly the same properties as every other part. If we consider, for example, a piece of granite, we readily convince ourselves that this stone is made up of parts having different properties. Beside the white, very hard grains there are others which are less hard and of a reddish colour, and between these there are rather soft, lustrous laminæ. In determining the properties of such a body, various results would therefore be obtained, according as the one or other small piece were examined.

We cannot, therefore, designate granite as a substance in the chemical sense, but rather as *a mixture of different substances*. As the characteristic of a substance in the chemical sense, we must demand that all portions into which it can be separated, exhibit the same properties. Such substances are called *uniform* or *homogeneous*. According to this, chemistry is the science of *uniform* or *homogeneous* substances. Simple as this conception appears, it required a long time, a time to be reckoned by centuries, for it to be formed with sufficient clearness, and the older history of chemistry as a science, might be called the history of the labours in the working out of this conception. The difficulty lay essentially in the fact that a sufficient distinction was not made between *mixtures* and homogeneous substances, with the result that the regularities which are peculiar to the latter but not to the former, were overlooked.

The Exactness of the Law of Properties.—The statement that sulphur is denser than water, and that it melts at a moderate temperature, can be made in a much more definite form by stating in what ratio the density of sulphur is greater than that of water, and at what temperature the fusion of sulphur occurs.

In a like manner, many other properties, and especially physical properties, can be expressed in definite measure, and the question arises, how do different samples of the same substance behave when a quantitative determination of their properties is made.

One might imagine that substances behave in a manner similar to the species of animals and of plants. The different specimens of one species, *e.g.* the common mouse, resemble, it is true, but do not completely agree with one another in size, growth of hair, colour, shape, etc. On the contrary, within certain limits, they show differences with regard to their properties. In like manner one could assume that the properties of different specimens of the same substance have closely approximate values, that these values, however, are not quite definite but vary within certain limits.

The innumerable investigations of this point which have been undertaken, show that the law of properties of substances holds not only approximately but *exactly*, and, therefore, *the measurable properties of different specimens of the same substance agree not only approximately but with all exactness.*

* It must be at once emphasised that it is not intended here to assert the *absolute* validity of the law. The absolute can never be the subject of experience, and, in fact, it is not admissible to employ the word absolute with reference to any relationship based on experience. The meaning of the assertion is rather this, that experience has, so far, shown no deviations which are beyond the limits of the possible error of observation. For, every measurement is exact only within a certain limit, and all conclusions which are drawn from these measurements can be valid only to this limit. Thus, the density of sulphur can be determined only with a limited degree of accuracy, and if the same value has been obtained with different specimens, the identity can be asserted only to this limit. The meaning of the assertion that the properties of different specimens of the same substance are the same, is only this, that within the limits of error hitherto reached, no differences have been found.

* The accuracy with which a magnitude is known must always be expressed in *fractions of its value*, and not as a concrete number. If in the measurement of a length the possible error amounts to 0·1 cm., this may express a large or a small degree of accuracy, according as the length is long or short. If we measure a distance of 20 metres to within 0·1 cm., the measurement is very exact, for the error amounts to, at most, $\frac{1}{20000}$th of its value. On the other hand, if a length of 3 cm. is known with such a limit of error, the measurement is not very exact, for the error can amount to $\frac{1}{30}$th of the measured value.

Pure Substances and Solutions.—To the law which has just been enunciated, it might be objected that although, on the whole, the substance which we designate, for example, by the name *water*, usually has the same properties, still the different kinds, such as, spring-water, rain-water, river-water, sea-water, show marked differences in their properties. However, these differences are not due to the *water*, but to other substances mixed with it which have been obtained from the surroundings in which the water occurs. The water can be separated from these admixtures by a simple expedient. Thus if we convert the different kinds of water, by heating, into vapour and reconvert, by cooling, the vapour into water, they all yield *pure* water with entirely concordant properties. The "impurities" remain behind in the vessel in which the water was evaporated.

All other substances with which chemistry has to deal, behave in a similar manner. By suitable treatment, which differs according to the nature of the substance, the latter can be freed from any admixtures which may be present. It then shows entirely identical properties, no matter from what source it has been obtained.

This case of impure water differs in one important point from the case of mechanical mixture, granite, mentioned before. Whereas in the case of granite the component parts can be distinguished even by the naked eye and, in other cases, what appears to the unaided eye as homogeneous is recognised under the microscope as a mixture, it is impossible in the case of impure water, as we have it, for example, in clear sea-water, to see the impurities. Under the strongest microscope we can recognise only transparent water, nor is there any other means by which we can show the presence of parts distinguishable in space. Sea-water is therefore a uniform substance; it is, however, not a *simple* substance in the chemical sense, for it can be separated, by the simple method of evaporation just mentioned, into pure water and salt, and the water so obtained has exactly the same properties as any other specimen of pure water.

Those substances which appear homogeneous but which, in the sense just explained, are not *simple* or *pure*, are called *solutions*. They are distinguished from pure substances chiefly by the fact that their properties from case to case, although similar, still differ by measurable amounts. These differences can have all possible values within definite limits, and by this fact, solutions can be distinguished from simple substances. They can be prepared by mixing simple substances in any proportions (within certain limits) and their properties change continuously with these proportions.

We shall find other differences when we come to discuss the general laws to which the simple substances, or substances in the chemical sense, are subject (Chap. VII.).

How many Properties are necessary for the Characterisation of a Substance?—Since the number of properties of a given substance is very large, and since also, two things can be designated as identical in substance only when they show entire agreement in *all* their properties, the task of testing whether two substances are the same or not, appears impracticable. And still, chemists are wont to identify substances with certainty after testing some few properties.

The surmounting of this difficulty is rendered possible by the fundamental law of chemistry already given (p. 6). This law, in its application to the present question, can be stated thus: *When two substances agree entirely in some few properties, they agree also with regard to all other properties.*

* This law, like all other laws of nature, is only a summary of observed facts. It does not prescribe that something *shall* happen, but only states what relations exist. For this reason the term "law," borrowed from jurisprudence, is not very suitable for expressing such regularities in natural phenomena, and it can be used without disadvantage only when the distinction, to which we have just drawn attention, between a law of nature and a civil law has, once for all, become quite clear.

* **Induction.**—The total number of cases classed under a law of nature can, evidently, be divided into two groups: a small one, embracing the cases which have been tested, and a very large one, to which belong the cases which have not been examined. For the task of testing a law in *all* cases in which it applies could not be undertaken, as the labour involved would be too great.

And, indeed, the necessity for such an examination is not felt; for, from the fact that in all cases which have been observed the law has been found valid, we may conclude with a high degree of probability that it will hold equally in those cases which may in future be investigated. This probability becomes all the stronger as the number of cases investigated increases, and the more the cases chosen for examination are independent of one another.

When the universal validity of the relationship has been established with a definite measure of probability, we are accustomed to regard it as a law of nature. However, the history we have just given of the genesis of such a law, implies that it cannot have the character of a *necessity*, and it is quite possible that, following on the many confirmatory cases, some should be found which do not conform to the law. The procedure which we have to adopt in such cases will be discussed later. For the present, we accept the statement that the laws of nature are conclusions as to probabilities, based on experience.

Such conclusions are called *inductive*, and the procedure by which they are obtained is called *induction*. The whole of natural science is built up of such inductive conclusions.

Sometimes the need has been felt of placing the laws of nature on a more certain foundation than is furnished by conclusions by analogy based on experience, since these afford no protection against the possibility of a contradictory case. However, this foundation is the most trustworthy that can be found at all, for the constant reference to experience prevents the investigator from replacing the actual relations by something imagined, which, although it may be as consequent as possible, still contains the possibility of deviation from actual facts. The natural sciences are, however, not called upon to represent the *possible* but the *actual* relations, and this they can do only by direct and continual reference to experience.

The Characteristics of Substances.—The number of different kinds of properties which can be measured or observed in a substance is very large, and increases continually with the advance of science. Even if it must be the task of chemistry to investigate *all* accessible properties in the case of *all* substances, there is still naturally a difference in the importance which is to be attached to the knowledge of the different properties. Especially for the first introduction to the science it is necessary to set a limit to the task. We shall, accordingly, examine more in detail, only a few of the properties, only so many as will serve, in the first instance, for the sufficient characterisation of the different substances and for the explanation of the relations between them.

Colour.—The most evident property of a substance, and the one most easy to observe, is its *colour*. It therefore forms a very important characteristic and is given in every description.

The colour of a body is due to the fact that a portion of the white light, by which we observe it, is absorbed while another portion passes through the body. It is, essentially, only rays of a definite wave-length or colour, that undergo absorption, and the transmitted light is therefore poorer in these rays. The colour which is produced when definite rays are withdrawn from white light, is called the *complementary colour* of these rays. The following are complementary colours :—

red	green
orange	blue
yellow	violet

When one of these six colours is absorbed, the complementary colour placed opposite it appears. The relation is *reciprocal:* if a substance absorbs blue light, it appears orange-coloured ; if it absorbs orange-coloured light, it appears blue.

The colours we have named represent only the large groups ; there are, in reality, an infinitely large number of colours and complementary colours.

Since the amount of light absorbed increases with the thickness of the layer through which it passes, the depth or intensity of the colour with which the substance appears is dependent on the conditions it offers to the passage of the light ; the thinner the layer the more faintly will it appear coloured.

This phenomenon can be conveniently shown by filling a wedgeshaped glass vessel with a coloured liquid (Fig. 1). When this vessel is held towards the light, there can be seen not only the deepening of colour with the thickness of the layer, but frequently, also, a change in the character of the colour.

* A thin layer of a solution of chrome-alum appears green; a thick layer, through which a strong light is allowed to pass, appears red.

In the case of liquids and gases the thickness of the layer is determined by the shape of the vessel, but in the case of *solid substances*, by the size of the pieces. In such a case the light enters into the piece and after undergoing reflexion at a posterior surface, passes out again in another direction. If we therefore view a fairly large number of pieces superposed on one another, the resulting colour will agree approximately with the coloration which light experiences on passing through a plate whose thickness is equal to twice the diameter of one of the grains. This is the reason that transparent, coloured substances appear lighter the smaller the pieces into which they are divided, and this circumstance must be taken into account in characterising the colour of a substance.

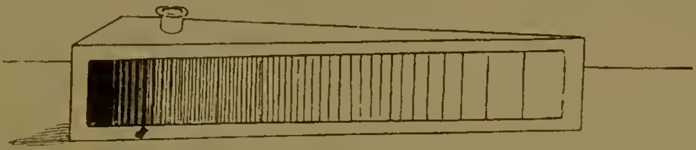
Fig. 1.

* A crystal of copper sulphate is dark blue. On being powdered in a mortar it gets lighter in colour the finer the powder is. Red crystals of potassium dichromate become yellow on being powdered.

Besides the light which comes from the interior of the body and which is changed by partial absorption, another portion reaches the eye directly reflected from the surface. This portion varies with the nature of the substance; in the case of transparent substances it is small, in the case of metals it is large. The *lustre* depends on this. The lustre does not play any great part in chemistry; only that of the very strongly reflecting metals, on account of its conspicuous nature, is used as a characteristic.

The Physical State.—A second, very important property of substances, is the way they fill space. One distinguishes between *gaseous*, *liquid*, and *solid* bodies, and denotes the differences occurring here by the term "physical state."

The three physical states denote the manner in which the bodies fill space. A solid body has a definite *form* and therefore also a definite *volume*.

A liquid body has no definite form; it has, however, a definite *volume*. It therefore fills a vessel in which it is placed only to the extent of its volume. Under the influence of gravity, the surface of liquids, in so far as they are not bounded by rigid walls, approaches the form of a horizontal plane.

Gases have neither a definite form nor a definite volume; they fill completely every vessel into which they are brought.

All these relations are further subject to special laws, which will be discussed in their appropriate place.

By means of the characteristics we have just given, we shall have, as a rule, no difficulty in determining whether a body is solid, liquid, or gaseous. If a body, when placed on a plane, retains its shape, it is solid; if it spreads out while, at the same time, a bounding plane, a *surface*, is formed on the top, it is a liquid; if it exhibits in no direction a bounding plane of its own, it is a gas. Between these three physical states there are, it is true, intermediate states which sometimes render the decision difficult, still these are not very frequent, and for the present we need not discuss them in greater detail.

A given body does not under all circumstances remain in the physical state in which it is at a given time; the physical state depends especially on the *temperature*. In this case, the general law holds that with rising temperature, a solid substance can become liquid or gaseous, and a liquid one gaseous, but never the converse. On the other hand, with lowering of temperature, gases become liquids or solids, and liquids become solids.

Although the sense in which the change takes place cannot be departed from, the liquid state need not, however, appear as an intermediate state between the gaseous and the solid. On the contrary, cases not unfrequently occur where with rise of temperature, solids pass directly into gases, and by cooling, gases pass directly into solids.

The laws which these transformations obey, will be discussed later (Chap. VII.).

Summary.—The conception of *substance* has been developed. By this name are designated the classes into which the inanimate bodies can be arranged according to their properties. Experience teaches that it is possible to arrange the naturally occurring or the artificially prepared bodies in classes so that the individual members of a class have the same properties. By properties in this sense are understood only those which are essential, and which cannot be given to or taken from the body at will. Experience teaches further that different bodies which belong to the same class or which consist of the same substance, agree not only approximately but exactly in their properties, so that the value of any property determined on one specimen may confidently be expected to be found in all specimens of the same substance.

The law of nature that classes can be formed of bodies which agree entirely with one another in their essential properties, is the fundamental law of chemistry.

If a body is to be subject to this law it must be *homogeneous*, *i.e.* it cannot be a mechanical mixture of different substances placed side by side. In such a case the law, indeed, holds not for the mixture but for the separate substances of which the mixture is composed.

Further, there are bodies which apparently do not obey this law, although they cannot be identified as mechanical mixtures. Such bodies can by simple means be separated into substances which obey the law. These are called *solutions*. Solutions are distinguished from pure substances by the fact that they can be compounded of two or of several components in every proportion (within certain limits), and that their properties vary continuously with the composition.

In conformity with the fundamental law, different specimens of the same substance agree entirely in their essential properties and differ in their properties from other substances. To determine whether two bodies are composed of the same substance, it is therefore, as a rule, sufficient to show that they agree with one another in respect of some few properties.

CHAPTER II

THE LAWS OF CONSERVATION

Change of Weight in Chemical Processes.—If we choose out for closer investigation some of the innumerable chemical phenomena which occur daily around us, we are struck with the *changes in the amount* of the substances taking part in the chemical process. When the stearin of a candle or the petroleum in a lamp burns, these substances seem to disappear entirely; the wood or coal burning in the fire leaves behind only $\frac{1}{20}$th to $\frac{1}{10}$th of its weight of ash. On the other hand, the sulphuric acid manufacturer obtains about three kilograms of sulphuric acid for every kilogram of sulphur converted. Changes of weight are therefore connected with chemical processes, and we have now to ask whether any generalisations can be made regarding these.

The examples we have just cited appear only to lead to the conclusion that in chemical processes diminution as well as increase in weight may occur. These are, however, not suitable examples for deciding the question, for the processes take place with the substances in free communication with their surroundings, especially with the air, and do not therefore allow of a balance being drawn up. To achieve this we must conduct the experiments in a closed space.

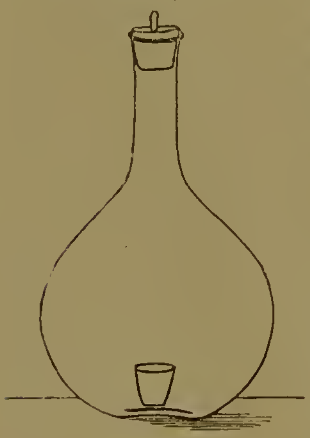

Fig. 2.

Experiments.—At the bottom of a large, thin-glass flask (Fig. 2), and resting on a layer of asbestos, is a small dish containing a little phosphorus. Phosphorus is a substance which requires only a slight elevation of temperature to cause it to take fire. The flask, closed by a ground-in stopper, is accurately counterpoised on the balance. The part where the phosphorous rests is then warmed, and the latter at once takes fire. In a short time the phosphorus becomes extinguished, while the flask has become filled with dense, white fumes.

On again placing the flask, after it has become cold, on the balance, *no change of weight is observed.*

* The flask must be allowed to cool before being reweighed. So long as it is warm it warms the air surrounding it, and this, ascending, raises the flask slightly upwards, and makes it therefore appear too light.

* Secondary circumstances of a similar nature, which more or less affect the result, are always met with in carrying out quantitative experiments. If an exact result is desired, they must be known and their influence either obviated or, if this is not possible, taken into account. The real difficulty of exact measurement lies in these secondary influences, and only by a varied experience, obtained by performing the experiments under as many different conditions as possible, can one succeed in so controlling these influences as to obtain exact measurements. Compared with this, the carrying out of the actual measurement is generally an easy matter.

The fact just described, that when combustion takes place in a closed space no change in the total weight is observed, although certain substances disappear and others are produced, is a general one. No matter what substances are burned under these conditions, a change of weight never occurs. This law also, is not restricted to combustions alone, but is true for all chemical processes. To illustrate this we may perform the following experiments.

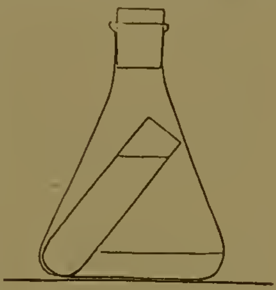

FIG. 3.

A wide test-tube is placed in a conical flask with wide mouth (an Erlenmeyer flask) (Fig. 3). Two substances which, on contact, react chemically with one another, are placed, one in the conical flask, the other in the test-tube, so that they are kept separate. The flask having been carefully closed and its weight determined, the substances are brought into contact by tilting the whole apparatus. Chemical reaction then takes place, generally accompanied by rise of temperature. On placing the apparatus, after cooling, again on the balance, *its weight is seen to be unchanged.*[1]

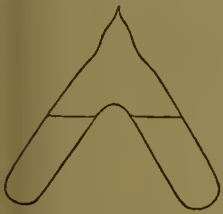

FIG. 4.

* Another method of performing this experiment is shown in Fig. 4. This method is more convenient, but the two-

limbed glass vessel must be specially made, whereas the vessels used in the first form of the experiment can be obtained ready made.

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[1] The following substances which give rise to chemical reactions recognisable by conspicuous changes, may be used, mostly in concentrated solution: potassium carbonate and calcium chloride (white precipitate), silver nitrate and caustic potash (brown-black precipitate), antimony trichloride and sodium sulphide (orange-red precipitate), zinc oxide and hydrochloric acid (clear solution), silver nitrate and ferrous sulphate (separation of metallic silver), hydriodic acid and iodic acid (separation of iodine), chloral hydrate and caustic potash (formation of two liquids).

* The experiment can be made still more clear, by making two pieces of apparatus whose size, contents, and weight are about the same, and mutually counterpoising these on a balance with the help of the necessary additional small weights.

* This arrangement of the experiment has the especial advantage that the buoyancy of the air, which acts on all objects causing them to appear as much lighter as the weight of the displaced air, is made equal on both sides. In this way, any changes in the density of the air do not affect the equilibrium, since the change in the upward force of the air amounts to the same on both sides. In carrying out exact measurements of this or a similar kind, use is always made of this artifice.

To prevent any possible escape of the substances formed, through the seams of the cork, the neck of the vessel is heated till the glass becomes soft, and the two portions are drawn apart; the connecting piece becomes contracted to a narrow tube which is then fused together. The contents are then enclosed entirely by glass and there is no longer any danger of an escape of substance. This method was formerly known as *hermetically sealing*, being so called after Hermes Trismegistos, a mythical chemist of ancient times. It is now generally known as sealing up in glass.

Conservation of Weight.—All the relations which have just been described can be summarised in a *Law of Conservation of Weight*, which states that the total weight of the substances taking part in any chemical process remains unchanged, that the weight, therefore, is *conserved*.

Nor is any physical process known by which such a change is produced. The law, therefore, holds universally.

The weight of a given substance is the force with which it tends to approach the earth. This force changes with the latitude and with the height of the place above the level of the sea, but obeys the law that it changes in the same ratio for all bodies. If, therefore, two bodies have the same weight at one place, they have also the same weight at all other places. The *ratios* of any weights are, therefore, constant and independent of locality.

The *mass* of a body is proportional to its weight. Bodies which have equal weights have also equal masses, and if their weights are different they stand in the same ratio to one another as the masses. Since the ratio of weights is independent of place, the masses of different bodies are, under all circumstances, in the same ratio as their weights.

If we unite this law with that of the conservation of weight in all processes, it follows that *the total mass of any system is not changed by any process which may take place within that system.*

These two laws are often designated as the law of the conservation of matter; there being understood, somewhat indefinitely, by matter, a something to which all the properties of the bodies are attached. On account of the indefiniteness of the conception of matter, there enters also into the corresponding law an indefiniteness which is not inherent in its nature, and which makes its content less clear than it really is. We shall therefore retain the more exact form of the law, which refers to weight and mass.

Some Mechanical Conceptions. Work.—Although the conceptions of mass and weight belong to physics, and a knowledge of them may therefore be presupposed, still, in the interest of later chemical considerations, we shall here briefly develop the most important points in this connection.

To bring about spatial changes on bodies, an exertion is necessary which we call by the name *work*. This exertion, or the work, depends on the nature of the body and the change of situation which occurs. A very simple case is afforded by the movements in the neighbourhood of the earth's surface.

If, for the estimation of work, I make use of the exertion of my muscles, I obtain the following result. To raise a body, work is necessary, and this is greater, the greater the height to which the body has to be raised. The raising through consecutive equal distances, requires, however, always the same work. For the rest, the work is dependent on the nature of the body, and increases with its weight.

In accordance with these relations, we define work as a magnitude which is proportional to the height h to which a body is raised, and to the weight w of the body. A magnitude which is proportional to two other magnitudes, is proportional to the *product* of these. If A denotes the work, we should, therefore, write, $A = wh$, putting the factor of proportionality equal to 1.

* It is sometimes asked if work is "actually" measured by this product. Such a question would be justifiable if we had already defined work in any other way. This is, however, not the case; we consider the conception of work as having been first established. We are, therefore, at liberty to define work by any other similar function. No one of these can be designated as wrong or right, but they will have different degrees of suitability, which will manifest itself in the greater or less simplicity of the corresponding laws. The definition of work given above has shown itself to be by far the most suitable of all the possible definitions.

When we raise a stone, we perform work on it, or we transfer work to it. On the other hand, the raised stone can, by falling down, perform work on other bodies. It thus loses work, and in order to bring it back to its former position, work must be again performed on it. We can therefore regard the work as being connected, in varying amount, with the stone, whose gain or loss in that quantity we shall calculate with plus and minus, as in the case of any other gain and loss. Work which is gained by the body is called positive, that which is lost by it, negative.

The Law of Conservation of Work.—In physics, many simple machines are described, such as the lever, the inclined plane, the wheel and axle, the pulley, etc., which have all the property that they allow of the transmission of work from one place to another. When such a machine (we shall consider, for the sake of illustration, a lever loaded with weights), is moved, it takes in work at one point and gives it out at another. Now, experience has taught that in all these machines, no matter how they are constructed, the work which is given out is never greater than the work that is put in; rather, the two are equal.

If we reckon the work put in as positive and that taken out as negative, the sum of the two is in all machines equal to zero.

This law can also be expressed thus: A given quantity of work can be neither increased nor diminished by a machine, but remains unchanged. There exists, therefore, a general *law of the conservation of work.*

The possibility of stating such a simple law, by defining work in the manner given above (p. 19), is the chief reason for choosing that definition. If, now, we bring the law we have just stated to the test of experience, we find a large number of cases which appear to be contradictory to it. We can continually observe that work disappears without other work making its appearance in its place. The work put into a wound-up clock is no longer there after the clock has run down, and fresh work must be put in to keep the clock in motion.

In this respect, however, we also know that clocks are different. An ordinary time-piece must be wound up every day; a better one, with equal weights and equal height of winding, will go for a week, and clocks can now be bought which go for more than a year with one winding up. By improvement of the mechanism of the clock, the loss of work can therefore be made less and less, and if we imagine the improvement continued indefinitely, the loss of work will converge to zero.

The law we have just stated, then, is valid exclusively for *ideal machines, i.e.* machines in which no work is lost. It represents, therefore, a *limiting law*, to which the actual phenomena certainly approximate, but which they never really fulfil. The justification for putting forward a law which is never fulfilled, is to be found in the fact that the amount of deviation from the law can be minimised to any desired extent; it represents, therefore, nothing essential, whereas the equality of work expressed by the law is the relation to which all machines can be made more and more to approximate.

In the enunciation of this law, we recognise the method of abstraction, which was described on p. 3. Disregarding the irregular deviations which can be minimised at will, we obtain the conditions with regard to which we can state simple relations.

The question as to what then becomes of the work that is lost in the case of imperfect machines, will be treated in detail later on (pp. 30 and 31).

Kinetic Energy.—Besides the cases we have just described in which work is lost through what is called friction, there are others in which work disappears, but where we cannot speak of friction, and where the loss cannot be made as small as we please. This occurs, for example, when we allow a heavy body to fall. It loses an amount of work corresponding to the height through which it falls. It has, however, passed into another condition, since it possesses a certain velocity.

By virtue of this condition, it can again give out work. This is seen in the case of the pendulum where the ball, after having been raised to a certain height, loses work as it falls in its circular path, and gains, at the same time, in velocity. Having reached its lowest position, it passes beyond it and gains work as it ascends; at the same time its velocity diminishes, and when this becomes zero, the pendulum has reached the same height as it was to start with. This process is then repeated over and over again.

* This description, also, holds only for the ideal extreme case in which friction is made to disappear. By suspending balls by means of exceedingly thin quartz fibres in a space rendered as vacuous as possible, pendulums have been made which, with one impulse, have carried out many thousand oscillations.

As is evident, one can interpret these processes by saying that, during the falling of the pendulum, work is transformed into something else which, during the second part of the oscillation, can again change into work. In the ideal case, this reciprocal transformation takes place completely.

Since experience has shown that many other cases occur where work is converted into something which can be reconverted into work, it is expedient to introduce a general name for this. This thing is called *energy*, and we include work also under this conception. Energy is, accordingly, work and all else that can be produced from and be reconverted into work. For example, there is a *chemical energy* which can also be converted into work.

The body which, through falling, has lost work, possesses in consequence of the fall, motion. Motion can be produced only through expenditure of work, or, generally, of energy. The special kind of energy which is produced in this case, may be suitably called *energy of motion* [kinetic energy].

Motion is measured by velocity, which is equal to the ratio of the distance through which the body has passed to the time required.

We have already (pp. 4 and 5) fixed the units in which these two magnitudes are measured; they are the centimetre and the second. The unit of velocity is therefore also determined; it is the velocity when one centimetre is passed over in one second, or something like the velocity with which a beetle runs.

If, therefore, in the case of a movement, we measure the distance s which is passed over in time t, the velocity c is given by the equation $c=s/t$.

Mass.—Even a very rough experiment will teach us that the same expenditure of work does not produce the same velocity in all bodies. On the contrary, the velocity which a thrown stone, for example, acquires, is, when the exertion is the same, so much the less the larger the stone. The kinetic energy, therefore, cannot be measured by the velocity alone, but another factor must be taken into account, which increases with the size of the body. In order to be able to talk of this factor, we call it the *mass*.

The relations between work, mass, and velocity, in the conversion of work into kinetic energy, can be very well investigated with Atwood's machine. This consists of two equally heavy bodies suspended by a string passing over a freely moving wheel. When one of the bodies is raised, the other sinks by an equal amount; the sum of the work performed and expended is in this case, therefore, equal to zero. A definite amount of work is now performed on this system, by placing on one side a small extra weight, and taking this off again after it has fallen a definite distance. We have in this case the following relations.

If we call two masses equal when equal work impresses on them equal velocity, we may, by combining such equal masses, prepare any multiple of them we please, and, therefore, *measure* the masses. If the masses are changed and the velocities which are produced in them by the same amounts of work are measured, these are found not to be proportional to the masses, but the *squares* of the velocities are proportional to the masses; or, the products of the masses and the squares of the velocities are, for equal amounts of work, equal. For different amounts of work, these products are proportional to the work.

Calling, therefore, the mass m and the velocity, as before, c, the expression mc^2 is proportional to the work which the displaced body has received and converted into kinetic energy. If A is the work, this relation will be represented by the equation $A=kmc^2$, where k is a factor depending on the units chosen.

Units.—We have not yet chosen the unit of work nor that of mass; we have, however, already the unit of velocity. We can therefore still make a decision as regards either the mass or the work.

Now, a mass is easily preserved and its relation to other masses easily measured, as we shall presently see. The storing, however, and measurement of a definite amount of work is much more difficult.

The decision has therefore been come to, to arbitrarily fix a mass. For this purpose there is used a piece of platinum preserved in Paris, which on account of the properties of the material and the care with which it is preserved, affords the greatest possible security against change. Also, as in the case of the unit of length, numerous exact copies of the same material have been made, whereby security against the chance loss of the unit is obtained.

As unit of mass there is used, not this piece itself, whose mass is called a *kilogram*, but the thousandth part of this mass, called the *gram*, or, abbreviated, gm. This mass is very nearly equal to the mass of 1 cc. of water at 4° C.

In the equation $A = kmc^2$, we have still to make a decision as to the factor k. For reasons which cannot be discussed here, this factor has been put equal to $\frac{1}{2}$, so that the equation reads $A = \frac{1}{2}mc^2$.

The unit of kinetic energy, in the first instance, is hereby fixed. If 1 gram moves with the velocity of 1 centimetre in the second (abbreviated cm./sec.), the energy amounts to $\frac{1}{2} . 1 . 1^2 = \frac{1}{2}$. The *unit* of kinetic energy is therefore double this amount. From the equation $A = \frac{1}{2}mc^2$ the *unit of work* is also equal to twice the work which can be gained from the kinetic energy of 1 gram having the velocity of 1 cm./sec. This unit is called an *erg*.

If we measure the work and also the kinetic energy in the units just fixed, experience teaches that in the conversion of work into kinetic energy, and *vice versa*, as much of the one disappears as is produced of the other, and that therefore the sum of the two is constant. *For these two forms of energy together, there is therefore also a law of conservation.*

Weight and Mass.—Having fixed the unit of work, we can now determine the factors of which it consists. In the case of a heavy body moving in the line of fall, the unit has been defined as the product of the weight and the distance. Now, not only in this case has work to be performed, but in many others also. All these cases agree in the fact that one of the factors of the work is a distance over which the body under consideration has to be moved. The other factor receives, generally, the name of *force*. A force, therefore, is present in those cases where a change in the position of the body cannot be effected without expenditure of work.

Since the unit of work has just been fixed, and the unit of distance, being a length, is given by the centimetre, we have no choice left of the unit of force; rather, this is the force which, acting over unit distance performs unit work, or 1 erg.

By means of this definition, we can easily calculate the value of gravity. This changes, as already mentioned, with the locality. In medium latitudes, it has the value such that 1 gram falling through 1 centimetre acquires the velocity of 44·26 cm./sec. If we call j the force of gravity acting on 1 gm., or its weight, the work performed in the movement through 1 cm. is equal to $j \times 1$, and this must be equal to the kinetic energy produced, viz., $j = \frac{1}{2} \times 1 \times 44{\cdot}3^2 = 980$. The force of gravity has the value 980; it is therefore nearly 1000 times as great as the unit of force.

Between the force of gravity and the mass of a body there exists a very remarkable relation, which, experimentally, finds expression in the well-known fact that all bodies, large or small, fall equally fast. This, it is true, is also only a limiting law, since it holds good only when the resistance of the air is excluded. Still, this condition can be fulfilled, experimentally, with great approximation.

Now, we have seen that the square of the velocity which a definite amount of work produces in a body is inversely proportional to the mass moved (p. 22). If then, as in the case of the free fall, two different bodies, falling through equal distances, acquire the same velocity, they can do so only if the amounts of *work* are proportional to the masses. And as the distances in both cases are equal, it follows that the *forces* must be to one another as the masses. The forces are, in the present case, called the weights. *In the case of heavy bodies, therefore, the weights are proportional to the masses.*

Expressed in formulæ, we have the following. Let the two masses be m_1 and m_2; by falling through equal distances, s, they acquire, as experiment shows, the same velocity, c. The amounts of work converted in both cases into kinetic energy, are w_1s and w_2s, where w_1 and w_2 are the weights of the bodies. The corresponding kinetic energies, $\frac{1}{2}m_1c^2$ and $\frac{1}{2}m_2c^2$ are also equal to these. From the two equations $w_1s = \frac{1}{2}m_1c^2$ and $w_2s = \frac{1}{2}m_2c^2$ there follows, by division, $w_1/m_1 = w_2/m_2$, or $w_1/w_2 = m_1/m_2$, which is the proposition we have just stated.

We cannot look on this result as "self-evident." So little is this the case that it is not even *intelligible*, *i.e.* one cannot see until now what connection this remarkable proportionality has with anything else. We are dealing here with a constant ratio between two quantities of a totally different kind. The masses have nothing directly to do with the weights, for they are only the measure of the kinetic energy which a body possesses when it has a definite velocity (p. 22). The weights, on the other hand, are the forces by virtue of which bodies tend towards the earth, and which find their expression in universal gravitation.

The Balance.—By reason of the universal proportionality between mass and weight, we can measure the one by means of the other. If we choose the unit of weight in such a way that it is equal to the weight which the unit of mass has, a determination of the weight gives directly the numerical value of the mass. This is the case when we take, as is universally done, the weight of 1 gram as the unit of weight.

Besides the gram there are also used its multiples and its subdivisions. Of these, the ones most employed are the kilogram, which is equal to 1000 or 10^3 gm., and the milligram or 10^{-3} gm. The other magnitudes (decagram = 10 gm., hectogram = 100 gm., decigram = 0·1 gm., centigram = 0·01 gm.) are but seldom used, and for scientific purposes should never be used at all.

For the chemist, now, neither the question, how much kinetic energy a body acquires under a given velocity (the mass), nor the question, what force it exercises on its support (the weight), is of supreme interest. An explanation is therefore necessary as to why the balance is, rightly, called the most important instrument in scientific chemistry.

When we buy substances for chemical purposes, for example, coal or food, which is of course done by weight, the mass and the weight of these things have likewise no direct interest for us. The determining factor is *that the chemical values*, the nutritive value or the heat that can be obtained by combustion, *are also proportional to the mass and the weight.* In mass and weight, therefore, we have a measure of the amount of chemical effect which the bodies can produce, and we determine the weight when we wish to measure the amount of chemical effect. How this is done in detail will be discussed later (Chap. VIII.).

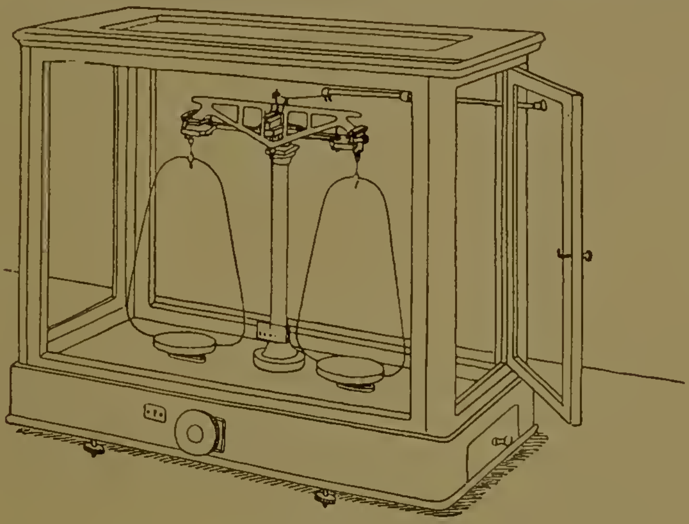

Fig. 5.

* The chemist's balance (Fig. 5) is a lever with two equal arms. Weighing consists in allowing the body whose weight is to be determined, to act on one end of the lever, while different weights of known value are made to act on the other end, until equilibrium is established, *i.e.* until the lever turns neither in one direction nor in the other.

* The balances used in ordinary life differ, essentially, only in *sensitiveness* from those used for scientific purposes. While an ordinary kilogram balance will still show differences of 1 gm., but not of

0·1 gm., the best scientific balances, when loaded with 1 kilogram, will show a difference of one hundredth of a milligram, or 0·00001 gm. The former has therefore a limit of error of 0·001, the latter of 0·00000001. The latter therefore allows of the determination of weight and mass ratios with proportionately greater exactness.

* This increase in the sensitiveness of the balance is effected by minimising, as far as possible, the hindrances to movement due to friction. The axis of rotation of the beam of the balance is formed by a knife-edge made of hard steel or agate, resting on a plane of hard stone. In the same way, the axes from which the pans for the weights and for the body to be weighed are suspended, are formed by knife-edges resting on planes. The three knife-edges must be parallel to one another and in the same plane.

* To prevent the knife-edges from wearing away too rapidly, they must be allowed to rest on the planes only during the time the balance is being used. Every good balance is therefore furnished with an arrangement for "arresting" it. This is so made that by turning a knob or a handle, the scale pans are first raised from the end knife-edges and then the beam from the plane on which it rests. The weights, etc. are placed on the scale pans while the balance is "arrested." On slowly "releasing" the balance, it can be seen in what direction the balance turns, and whether the weights have to be increased or diminished.

* Since a moderately good balance detects amounts even as small as 0·0001 gm., one would require weights of a corresponding value, in order to finish the weighings. These are very inconvenient to handle, and chemical balances are therefore furnished with another arrangement for determining the smallest weights. The balance beam, from the middle to the end knife-edges, is divided into ten parts, and there is a contrivance by means of which a weight of 0·01 gm., which from its form is called a "rider," can be placed at any point on the beam. According to the law of levers, the effect of the weight is smaller, the nearer it is placed to the axis of rotation. If, for example, the rider is placed at a distance from the axis equal to $\frac{3}{10}$ths of the length of the beam, it acts as a weight of 0·003 gm., and every tenth of the beam corresponds to one milligram.

* In weighing, therefore, it is necessary to counterbalance a body only to within 0·01 gm. with weights, and then to move the rider till complete equilibrium is obtained. The tenths and hundredths of the beam length give the milligrams and tenths of a milligram which have to be added to the weights.

* The production of equilibrium is shown by a pointer attached to the beam of the balance and moving in front of a scale. Since a good balance does not remain at rest but continues for a long time oscillating like a pendulum, one observes the extreme positions of the pointer, or the deflections, and takes the mean of these.

* To complete the weighing it is not expedient to obtain the final adjustment by shifting the rider, as we have just assumed for the sake of clearness. Rather, use is made of the fact that the change of the position of rest is proportional to the excess of weight. If the change of zero caused by a change in the weight of 1 milligram has been determined, it is only necessary to set the rider at the nearest whole tenth to be able to calculate, from the deviation of the point of rest now obtained from that when the balance is unloaded or the zero, the fractions of a milligram which would make the equilibrium perfect.

Density and Extensity.—The aids to the definition and measurement of masses and weights just considered, form the basis for the determination of an important property possessed by all substances, which, by reason of the great variation of its value from substance to substance, is largely used for distinguishing and characterising these. This is the *density* and the *extensity* (*Räumlichkeit*).

When defining the conception of "substances," we expressly omitted to take the mass into account (p. 5), as also the space occupied by a given piece of the substance. Since, however, these two magnitudes vary simultaneously and in the same degree, their *ratio* is a definite property of the substances, and, according to the general law, must always have the same value for a given substance under given conditions.

If we denote the mass of a given specimen of a substance by m, and the space which it occupies, or the volume, by v, we can form the two expressions m/v and v/m. The former, the mass in unit volume, is called the *density* or the specific gravity, the latter, the volume of unit mass, is called the specific volume; we will call it the *extensity*.

The units in which these magnitudes are measured have already been fixed: the unit of mass is the gram, and that of volume is the cubic centimetre. Since the mass is expressed by the same number as the weight, the density is equal to the weight of the body in grams divided by its volume in cubic centimetres; hence the name specific gravity. The extensity has the reciprocal value. If we call the density d and the extensity e, we have the relation $d = 1/e$ and $e = 1/d$.

Of these two expressions, the density has, as a rule, the preference, since, on viewing a body we first estimate its volume with the eye, and obtain an idea of its weight only when we have taken it in the hand. One refers, therefore, involuntarily, the weight to the volume and not the volume to the weight. For scientific purposes it is better to employ the opposite relation. For the mass is an unchanging magnitude in a body, whereas volume depends on pressure and temperature, and it is more rational to refer the variable quantity to the invariable than conversely.

In accordance with the common custom, however, the densities shall in this book also receive the foremost place.

Measurement of Density and Extensity.—To determine the ratio between volume and mass, a measurement of both magnitudes for the given body is necessary. The mass is determined by weighing (p. 25); the determination of the volume varies with the physical state of the body. It is easiest in the case of liquids.

The most direct method consists in filling a vessel of known capacity with the liquid, and determining its weight. Such vessels can be made of various kinds according to the accuracy aimed at. A very rapid and convenient method consists in the use of a vessel of the form shown in Fig. 6, called a pipette. It consists, essentially, of a narrow tube, widened in the middle, and is filled by dipping one end in the liquid and sucking at the other. On the upper tube is a circular mark forming the limit of a definite cubic content, which usually amounts to a round number of cubic centimetres. In filling, a slight excess of liquid is sucked up, and then, closing the upper end of the pipette with the finger, the excess is cautiously allowed to run out till the liquid stands at the mark. The filled pipette is placed on the balance in a horizontal position, resting on a bent wire carrier (Fig. 6). If the empty pipette with the carrier has been previously counterpoised, the increase in weight gives directly the weight of the liquid.

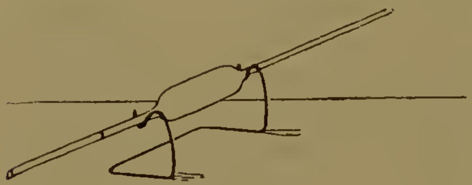

Fig. 6.

The determination is simplest when a pipette of exactly 1 cc. capacity is used, and a weight made which counterbalances the empty pipette along with its carrier. In accordance with commercial use, such a weight is called the *tare*. The extra weight is then directly equal to the density of the liquid, since, of course, the divisor, the volume, is equal to 1. Such a determination can be carried out with an error which is less than 0·001.

Another method is based on the principle of Archimedes, according to which a body sunk in a liquid experiences an upward pressure equal to the weight of the liquid displaced. A glass sinker, closed on all sides and hung by a hair or fine platinum wire, is counterpoised on the balance; it is then sunk in the liquid to be investigated and the decrease in weight, or the upward pressure, determined. The volume of the sinker is determined by conducting the same experiment in water; the upward pressure in grams is equal to the volume in cubic centimetres (p. 23). If this experiment is not performed at 4° C., one finds from the tables of the expansion of water the weight of 1 cc. at the temperature of the experiment, and divides the upward pressure found by this.

In this case also, it is most convenient to make a sinker whose volume is exactly equal to 1 (or to 10) cc. The loss of weight gives then, directly (in the case of 10 cc. after moving the decimal point one place to the left), the density of the liquid.

Finally, for rapid determinations of the density, the *hydrometer* is used. This consists (Fig. 7) of a glass float terminating at the top in a narrow tube within which there is a scale. The instrument is so made that it floats perpendicularly in the liquid to be investigated. Since a floating body sinks to such a depth that the weight of the liquid displaced is equal to the weight of the body, the position of rest varies with the density of the liquid, and the scale is read at the point where the stem passes through the surface of the liquid. The scale is generally graduated so as to allow of reading off the densities directly. However, other scales are in use, which have different names according to their inventors, and whose zero corresponds to the density of water. For scientific purposes these have no importance.

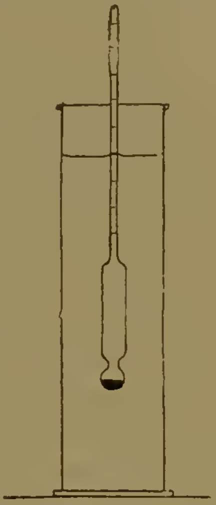
FIG. 7.

Densities of Solid Bodies are determined by two chief methods. Generally, they are weighed first in air and then in water or other liquid. The first weighing gives the mass, the second the loss of weight or the upward pressure, and from that the volume. When the second weighing is carried out in water, the upward pressure is equal to the volume (the influence of temperature being allowed for; *vide infra*). If another liquid must be used, as in the case of substances soluble in water, its density must first be determined by one of the methods just described, and the upward pressure must be divided by the value of this. For the volume of the liquid is equal to its weight divided by its density (p. 27).

* In carrying out such experiments, regard must often be had to the fact that the bodies are not present in large pieces, but in grains or small pieces. In this case, they are weighed under water in an open vessel of glass or platinum, as in Fig. 8. The weight of the vessel under similar conditions, viz., immersed in the liquid, must, of course, be previously determined.

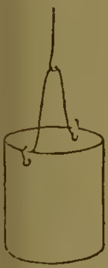
FIG. 8.

Another method, employed especially with small quantities, consists in mixing together two liquids, one of which is denser, the other less dense than the solid to be investigated, so as to give a liquid whose density is equal to that of the solid body. This identity is shown by the fact that the body neither rises nor sinks, but remains suspended in the liquid. The experiment is carried out by placing the body first of all in a small quantity of the lighter liquid, in which it sinks to the bottom. There is then cautiously added so much of the other liquid till the suspension is produced. Generally one will add rather too much of the second liquid; the error can, however, be easily rectified by the addition of some of the lighter liquid.

When suspension takes place, the density of the mixture is determined by one of the methods described on pp. 28 and 29.

* As a heavy liquid there is used methylene iodide or acetylene tetrabromide; as a light one, benzene or toluene. These liquids can be obtained commercially.

The necessary information for the determination of the density of gases will be given later (Chap. V.).

Influence of Pressure and Temperature on the Density.—It has already been mentioned that although the mass experiences no change in any process, the volume is dependent both on the temperature and on the pressure. The density of a substance will therefore likewise vary with these circumstances; and in order to make a statement definite, the values of both of these must be given at the same time.

The influence of pressure, now, is generally very small. The volume of liquid substances is diminished only by some hundred thousandths of its value when the pressure is increased by 1 atmosphere, and in the case of solid bodies this influence is in most cases still smaller. It is therefore necessary to have regard to this variability only in the case of very exact investigations.

The influence of temperature is, however, much greater. The volume of a given body is (with few exceptions) increased by a rise of temperature. The amount of increase is very different in the case of different substances, and is in general greater for liquids than for solids. As a rough estimate one can assume that liquids expand by about one thousandth of their volume for every degree of rise. This is, however, only a very rough approximation, since the amount varies not only from liquid to liquid, but also with the temperature itself. The higher the temperature, the greater is the relative increase of volume with the temperature.

In the case of accurate statements of the density of liquids, therefore, a statement of the temperature is necessary. Approximate statements, such as will often be made in this book, refer to room temperature, say 18° C.

The other Forms of Energy.—In the discussion of perfect and imperfect machines (p. 21), there still remains the question, what becomes of the work which in imperfect machines disappears. In order to find an answer to this, let us make a machine which is as imperfect as possible, so as to make the effect produced by this quality as clear as possible. In other words, we increase the friction to such a degree that the machine consumes almost all the work that is put into it and gives out only a small amount of it in external work.

The result of such an increase of the friction is seen in the case of badly kept axle bearings in driving engines, vehicles, etc. Those parts where the friction is great *become warm*. A more exact investigation shows that the amount of heat thus produced is proportional to the work lost. Since, on the other hand, work can be again obtained from heat, as in the case of steam engines, it follows that heat is something which can be obtained from and be reconverted into work. In accordance with what was laid down on p. 21, heat must be called a kind of energy.

If the heat be measured in units which are equal to the amount obtained from an erg of work (p. 23), it is found that the heat produced in an imperfect machine is always equal to the loss of work. If, then, the heat be also reckoned, the total amount of energy converted is equal to the work put into the machine, and the law of conservation again holds good.

These considerations can be extended. There are other forms of energy which are produced from and which can again be converted into work. A familiar example is *electrical energy* which, by means of dynamos, can be produced from work and be again converted into work or into heat, etc. Each of these forms of energy can be measured by taking as unit the amount produced by 1 erg of work.

Another example is *chemical energy*. Combustion (p. 16) is a chemical process. By the combustion of coal in steam engines by far the greater part of the work is produced which is used in the arts and manufactures; this work is therefore a product of transformation of chemical energy.

For all these forms together, the law of conservation holds. If in a closed system transformations of energy take place, the sum total of energy remains, at each moment, unchanged, the production of one energy being accompanied by the simultaneous disappearance of an equivalent amount of another energy; and conversely, no energy disappears without an equivalent amount of another form being produced. An essential supposition made here is that all the forms of energy are measured in the same units, *e.g.* the erg.

* The more exact explanation of this exceedingly important law will be given in the course of our further discussions. We shall here still touch only on the question, how it is possible to discover such a wide and comprehensive law and to prove it inductively, *i.e.* support it with a sufficient number of examples. The answer is an historical one.

* In former centuries numerous mechanicians—some of them exceedingly skilled—busied themselves with the problem of perpetual motion, *i.e.* with the construction of a machine which should keep itself in motion, and at the same time perform external work. All their endeavours remained fruitless, and it looks as if the work of all these industrious and ingenious men had been in vain.

* If, however, from this failure we draw the definite conclusion that a *perpetuum mobile* is an impossibility; that it is, therefore, not

feasible to create work out of nothing, and that machines at best can give out only the amount of work which is put into them, we obtain the positive law of the conservation of work in perfect machines. The further question as to where the lost work remains in imperfect machines, has led to the recognition that work can be converted into other forms of an equivalent thing, which is called energy ; and as the final result of the impossibility of perpetual motion there is developed the law of the conservation of energy—one of the most important laws of all natural science.

* Similar developments of fruitless labour into positive laws can be recognised in other parts of natural science, and we shall at a later time have to occupy ourselves with such cases (cf. Chap. IV.).

Summary.—The production and disappearance of substances during chemical processes raises the question, whether these changes obey any laws ; and it is found as a universal experience, with no exception, that the total weight of the substances taking part in any chemical process remains unchanged. The total weight of the new substances produced is equal to the combined weight of the substances disappearing.

There holds, therefore, for all chemical processes (and for all other known processes likewise) the *law of the conservation of weight.*

The mass of a given body is proportional to its weight, the ratio of mass to weight being, for all bodies, independent of their other properties, constant at a given spot. Hence there also obtains for all processes, the chemical ones included, the *law of the conservation of mass.*

The two magnitudes, weight and mass, have no direct relation to one another, and the law of their proportionality is a purely empirical law.

An indirect relation between mass and weight is found by the aid of the conception of work. Denoting by this name the product of a force and the distance over which it acts, the law can be stated, for the simple "machines," that in the limiting, ideal case, the work can be neither increased nor diminished by such machines. There exists, therefore, for them a *law of the conservation of work.*

In special cases, work apparently disappears. In these cases it can always be shown that something else is produced at the same time which is proportional to the work which has disappeared, and which can be reconverted into work. If we denote all such things as can arise from and be converted into work by the name *energy,* and if we measure the different kinds of energy in units based on the conversion of a definite amount of work taken as the unit, there holds good, quite universally, a *law of the conservation of energy.*

There are various kinds of energy. Besides work in the sense just denoted, kinetic energy, electrical energy, chemical energy, heat, were characterised as various kinds of energy.

The unit of energy is called the *erg*. It was defined as twice the energy contained in 1 gram of any body when it has the velocity of 1 centimetre in 1 second.

If the body has the mass m and the velocity c, both measured in the units just given, its kinetic energy is equal to $\frac{1}{2}mc^2$.

When 1 gram falls through 1 centimetre, under the influence of gravity, it acquires the velocity of 44·26 cm./sec. Its kinetic energy is, therefore, equal to 980 ergs. This has been produced from the work of gravity, which is equal to the product of the force of gravity and the distance. Since the latter is equal to unity (1 cm.), the former must be equal to 980. The force with which gravity acts on 1 gram is, therefore, equal to 980 units.

A body of n grams acquires the same velocity, since, as experiment shows, all heavy bodies fall equally fast. Its kinetic energy, therefore, amounts to 980 n. Accordingly, the force of gravity acting on n gm., amounts to 980 n units.

In chemistry, weight and mass have a special importance, from the fact that the chemical energy which can be obtained by the transformation of any substance, is proportional to its weight and its mass. Since the value of substances used for chemical purposes, *e.g.* articles of food or fuel, are measured according to the amount of chemical energy which can be obtained from them, the weight is also a measure of the chemical value of different quantities of the same substance.

In conclusion, we may group together the units we have selected for the measurement of the different magnitudes. These units are universally used in science, and are called *absolute units*.

Unit of Time	Second	sec.
,, Length	Centimetre	cm.
,, Mass	Gram	gm.
,, Energy	Erg	e.

The last two units are not independent of one another since, when one of them is given, the other can be determined from it with the help of the first two.

From these fundamental units, compound units are derived by uniting the proper magnitudes. Thus, the unit of velocity is the velocity of 1 centimetre in 1 second, 1 cm./sec. The unit of force is that which acting over 1 cm. performs the work 1 e., and is therefore represented by 1 e./cm. The units of area and volume are given by cm.^{2} and cm.^{3} The unit of density is 1 gm./cm.^{3}; that of extensity 1 cm.^{3}/gm.

CHAPTER III

THE PHENOMENA OF COMBUSTION AND OXYGEN

Combustion.—Of the chemical processes which unceasingly take place in our surroundings, the *phenomena of combustion* form one of the most extensive and important groups. From remotest times, therefore, they have attracted interest, and a large part of scientific chemistry has developed around them.

Combustion, such as that of coal in the fire or of petroleum in the lamp, possesses in a marked manner the peculiarity of chemical processes, for in these cases the burning substances disappear and new substances are produced.

Apparently, combustions take place in such a manner that the substances disappear either completely, as in the case of petroleum, or at all events, for the greater part, as in the case of coal. For the ash which in the latter case remains behind amounts to only a small fraction of the weight of the coal.

That combustions, however, take place in which the converse is the case can be shown by many examples. Place on the one scale-pan of a balance a small wire tripod, lay thereon a piece of fine wire-gauze, and shake out on this a small heap of fine iron powder. On warming the edge of the heap with a flame the iron begins to glow, and it gradually burns, forming a blackish, coherent, friable mass, which has quite other properties than the iron, and is, therefore, a new substance.

Since, under these conditions, the combustion of the iron can be observed only close at hand, we can make it visible at a distance by sprinkling some of the iron powder in the flame. Each particle then burns, forming a brilliant, star-shaped spark. On a sheet of paper placed underneath, particles of the same blackish mass as is produced by the burning of the iron on the wire-gauze are found.

While the combustion is taking place on the wire-gauze, the side of the balance on which the iron is, is seen to become heavier, and at last strikes with some force against the base. The combustion of iron takes place, therefore, with increase of weight.

Is Increase of Weight on Combustion Universal?—Since the first supposition, that combustion and decrease of weight always go hand in hand, does not turn out to be true, one may suppose that the opposite is the case, *i.e.* that increase of weight always occurs. For it follows from the law of conservation of weight, that burning petroleum and burning alcohol do not disappear into nothing. New substances must, therefore, be produced, and the following experiment will readily convince one of this. Take a large, dry tumbler and hold it over a flame so that the flame burns inside. The tumbler is then seen to become immediately covered with a film which has exactly the appearance of the film of moisture which forms on cold window panes. On closer investigation one can convince oneself that the film consists of water. Since this phenomenon does not occur when the tumbler is held over the unlit lamp, it follows that *water* is formed in the flame.

Further, if a similar tumbler be rinsed out with lime-water and then held in this condition over the flame, a white solid is formed in the lime-water which looks exactly like chalk. This phenomenon also occurs only when the lamp is lit.

* The lime-water for this experiment is prepared by shaking lime with water, and then allowing the milky liquid to stand in a closed bottle. In a few hours the lime sinks to the bottom, and the clear, supernatant liquid is then poured off into another bottle. As a rule, it thereby again becomes milky, and must stand some time to become clear.

These experiments show that, although in the combustion of the above liquids, the latter certainly disappear, new substances are produced, which escape direct observation only from the fact that they occur as gases.

Processes, by means of which the presence of certain substances can be detected, such as the formation of the film on the tumbler and of the white solid in the previously clear liquid, are called *reactions*, and the substances necessary for them, *reagents*. The formation of the film is a reaction for water vapour, and lime-water is a reagent for another substance which is also formed in the combustion of petroleum or of alcohol.

To give, then, a proper answer to the question, whether in the combustion of petroleum or of stearin an increase or diminution of weight occurs, care must be taken that the gases formed do not escape into the air, but are held fast. This is effected by means of a white substance which is sold under the name of caustic soda, and is formed into rods or broken into irregular pieces. With this substance the upper part of a lamp cylinder is loosely filled, a piece of wire-gauze fixed into the cylinder preventing the caustic soda from falling down. The cylinder is then placed on the balance in such a way that a small lamp or a candle can be placed underneath it (Fig. 9).

When the whole has been brought into equipoise the lamp is lit. In a short time that side of the balance on which the lamp is, sinks, thus proving that the petroleum and the stearin on combustion are converted into substances which are heavier than the part of the combustible substance which disappears.

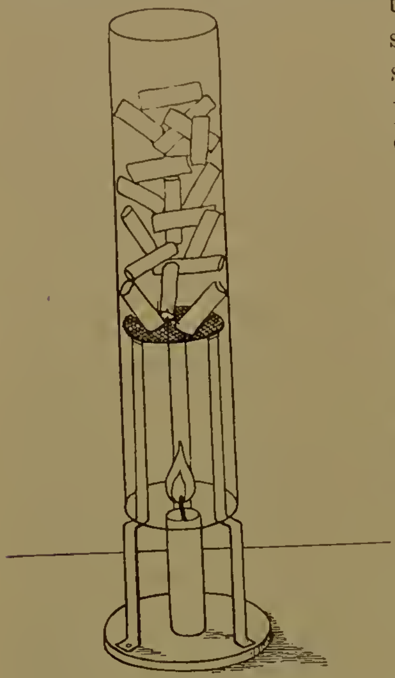

FIG. 9.

From these experiments we can draw the general conclusion that combustion consists in the chemical action of the combustible substances on some other substance which combines with them to form new substances. For, according to the law of the conservation of weight, the increase of weight can be produced only by the addition of another ponderable substance to the substances undergoing combustion.

This substance will be sought for in the air, since, in the case of the processes we are considering, there is no possibility of the access of any other ponderable substance.

Behaviour of the Air during Combustion.—For the purpose of getting a more exact knowledge of the process of combustion in this direction, we must shut off the process from the rest of the outside world in such a way that we can investigate all the changes which occur in the participating substances. We therefore carry out the combustion in a closed space, in a glass flask.

The first thing that we notice here is, that in a given volume of air it is not possible to burn any quantity of oil, but that the amount burned is greater, the greater the volume of the air. There is, therefore, something contained in the air which is necessary for combustion.

The air, however, does not consist entirely of this something. No matter what substances are burned in a given quantity of air, one never succeeds in using up the whole amount of air; on the contrary, about $\frac{4}{5}$ths of it remain behind. In this residue, combustion can no longer be produced, and closer investigation shows that the gas remaining has other properties than the air. From this it may be concluded that the air is not a simple substance, but a mixture (a solution), consisting of a substance which is necessary for combustion, and of another which does not effect combustion.

Oxygen.—That the power of the air to support combustion depends on the presence of a gaseous substance which does not constitute the whole air, but only about $\frac{1}{5}$th of it, was stated by the chemist, Scheele (born at Stralsund), towards the end of the eighteenth century. Scheele confirmed his opinion, which was opposed to the then existing ideas of the "elementary" nature of the air, by showing how to prepare a substance which had the power of supporting combustion in a much higher degree than ordinary air, and which left behind no residue incapable of supporting combustion.

Scheele obtained his gas, which he called *fire-air*, by strongly heating the substance well known by the name of *saltpetre.* He afterwards obtained it in the same manner from the mineral pyrolusite.

Independently of Scheele, the same substance was discovered somewhat later by Priestley, who prepared it by strongly heating a red-yellow substance called oxide of mercury.

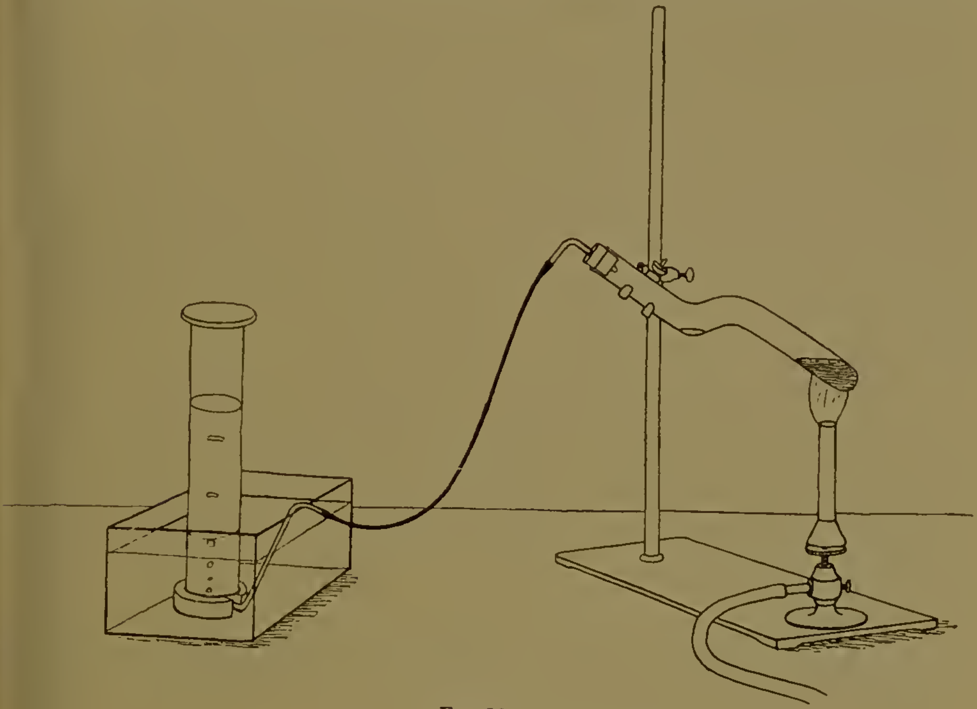

Fig. 10.

The last experiment is the most convenient for repetition. The red-yellow powder (oxide of mercury) is placed in a bent tube of hard glass (Fig. 10). The tube is closed by a perforated cork, carrying a narrow tube with indiarubber tubing attached. On heating the tube containing the oxide of mercury, this substance first becomes darker, almost black, in colour. After some time a film with a metallic lustre is formed on the tube near the heated part. If the end of the gas-delivery tube is placed under water bubbles of gas are seen to rise. This might be taken for air, which is caused to expand by the heating, and partially escapes from the tube. We can readily convince ourselves, however, that the gas is not ordinary air; for if a splinter of wood which has been lit and then blown out, so that only the charred end glows feebly, be brought to the mouth of the tube, it at once bursts into flame. The gas which is evolved can be collected by filling a vessel with water and inverting it in the trough in such a manner that the opening remains under water. On allowing the gas bubbles to pass from the tube into the mouth of the vessel the water is displaced by the new gas, and after some time the vessel is filled with it. The process goes on so long as there is oxide of mercury present. This has, however, in the meantime diminished in amount, and after some time disappears entirely. At the same moment, the evolution of gas ceases.

Properties of Oxygen.—If we examine the gas thus obtained, we cannot, by its external appearance, distinguish it from air. Like air, it is colourless; proves, on appropriately testing it, to be odourless and tasteless; from the manner of its preparation also, it is evident that it is, like air, insoluble or only slightly soluble in water. That it is, however, different from air is shown by its already known behaviour towards glowing wood. Exact investigation, also, shows that its density and its other physical properties are distinctly different from those of air. We have, therefore, ground for considering the gas evolved from oxide of mercury to be a substance of a special kind. Such, as a matter of fact, it is, and it is called oxygen.[1]

Decomposition of Oxide of Mercury.—Let us now investigate more closely the process by which we have obtained oxygen. As we see, the oxide of mercury has completely disappeared. Along with the oxygen, however, a liquid substance with a metallic lustre has been produced; this has been deposited in the fore part of the tube, and exhibits the properties of mercury. Besides these, nothing else can be detected.

The oxide of mercury has, therefore, been converted into oxygen and metallic mercury. If the weight of the oxide of mercury, of the mercury, and of the oxygen be determined, it is found that the weight of the first is equal to the sum of the other two. In accordance with the law of the conservation of weight, we shall say that the oxide of mercury has, under the influence of heat, been transformed into mercury and oxygen, and we may add that no other substance can have been produced in the process. We can therefore write the equation:

$$\text{Oxide of mercury} = \text{mercury} + \text{oxygen},$$

where the sign of equality signifies that the substances on either side of the sign can be transformed into one another.

One often finds the expression used that oxide of mercury *consists* of mercury and oxygen, since the former can be converted into the latter. However, oxide of mercury exhibits the properties neither of mercury nor of oxygen. Since a substance is characterised only by its properties, such a statement as the above has no real meaning, and is only a short inaccurate method of expressing definite regularities which will be discussed later (Chap. IV.).

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[1] The name oxygen (acid producer) belongs to an olden time, and is the expression of a former, erroneous opinion that this substance is contained in all acids and is essential for their properties. Even after the recognition of the falsity of this view, the name was retained.

This method of expression is, however, so generally used that we must retain it for the sake of intelligibility, though with the reservation just made.

Combination.—The process of the conversion of oxide of mercury into mercury and oxygen can be reversed. By heating mercury in contact with air, *i.e.* with the oxygen of the air, to about its boiling point, it is converted into oxide of mercury. The process, however, requires days in order to yield an appreciable amount of oxide of mercury.

As a single substance is hereby produced from two different substances, the process is called a *combination;* the reverse process, the conversion of one substance into two—oxide of mercury into mercury and oxygen—is called a *decomposition.* In the same way, mercury and oxygen are called the *constituents* of oxide of mercury, and this, a *compound* of the two other substances. It is looked upon, therefore, as a *composite* substance with regard to its constituents; still one may be again reminded of the reservation we have just made.

Quantity Relations.—Returning to our experiment, we can raise the question as to the quantity relations of the participating substances. From the experiences of common life, one will be inclined to assume that in the conversion of a substance A into a substance B, the amount of B obtained will diminish and increase in the same ratio as the amount of A used. However, from the same experiences, one would conclude that although the "yield" would on the whole agree with this rule, it would, in individual cases, show more or less deviation from it.

Let us perform suitable experiments by decomposing various accurately weighed-out amounts of oxide of mercury and measuring the oxygen evolved. (The necessary precautions to be taken here will be presently discussed; *vide* Chap. V.). We find that *the ratio of the amount of oxide of mercury used to the amount of oxygen obtained is constant, not only approximately but with all the accuracy with which we can allow the measurement.*

The relation which we here meet with is a case of a general law of nature.

When one substance is converted into another, there exists a definite, invariable relation between the amount of the substance disappearing and that of the substance produced.

We can at once extend this law and say that when two substances combine with one another to form a third substance, an invariable relation also exists between the two substances. For the weight of he substance produced stands, in accordance with the law just stated, in a constant relation to that of the substance which disappears. This weight is, however, equal to the sum of the weights of the combining substances. If the two separate weights are proportional to their sum, they are also proportional to one another.

In symbols, the law can be represented thus. Let the amounts of the combining substances be A and B, and the amount of the substance produced or the compound be C. Then, according to the first law, $A/C = \text{const.}$, and $B/C = \text{const.}$ From this there follows, by division, $A/B = \text{const.}$, which had to be proved.

What has here been stated for two substances which combine with one another holds for any number of substances; the *law of constant combining proportions* is universal.

The accuracy of this law has been subjected to a very careful test by various investigators, both the source or the method of preparation of the participating substances and the conditions of the transformation being changed as much as possible. The result obtained was similar to that in the case of the law of the conservation of mass, and no one has succeeded in showing deviations from the law. On the contrary, the relations were found to be invariable within the same limits of error as the quantity determinations themselves could be carried out. The law of invariable transformation ratios belongs, therefore, along with the law of the conservation of mass, to the few laws which, within the bounds of our present knowledge, can be designated as entirely exact.

Deductive Derivation of the Law of Constant Proportions. —The law of the invariability of the combining proportions, which we have just obtained empirically, can be regarded as a consequence of the previously stated law of the definiteness of the properties attaching to substances, if we reckon as properties all relations in which the substance can be placed with regard to others. For the proportion in which one substance is produced from other substances certainly belongs to these relations, and it appears quite proper to expect that when a third substance with quite definite properties is produced by the interaction of two substances, the amounts of the reacting substances necessary for this result cannot interact in arbitrary proportions, but must do so in *definite* proportions.

* Such a method of argument is frequently used in science for the purpose of deriving unknown relations from others already known. The method is called *deduction*, and a science which is based entirely or chiefly on such a method is called a *deductive* science. As is evident, a double possibility of error attaches to the deductive conclusions. Firstly, these conclusions share all the uncertainties attaching to the assumptions from which they are developed. Secondly, to these have to be added the uncertainties which may lie in the method of derivation. Formal logic, it is true, teaches how to avoid gross errors of the latter kind; less apparent errors, however, which are due especially to

the varying nature of the conceptions employed, and to the incompleteness of the distinctions made, can often be avoided or discovered only with difficulty.

* In the natural sciences, now, there is an invaluable means of testing deductive conclusions: *their demands are compared directly with experience.* Thus it would have been quite possible for a meditative investigator to derive the law of constant combining proportions from the empirically formed conception of a substance endowed with definite properties. He could then have stated this law as a deduction from the former one; it would, however, have obtained validity in science only when he or some other investigator had proved the correctness of the deduction by a number of appropriate measurements.

* From this it would appear as if the method of deduction could be entirely dispensed with, since the results, as we have seen, must be tested and confirmed by experience before they are acknowledged. The discovery of new laws could, indeed, be left entirely to experience. Against this, however, there is to be said that the empirical discovery of laws would be too dependent on chance, whereas the drawing of conclusions from existing laws offers a rational method for the discovery of new ones. But further, it is of the highest importance to know the interdependence of the different laws, so that if limitations or errors are found in a law, one may be able to judge of the bearing of these on other laws. This interdependence of the laws can, however, be ascertained only by the deductive method. This forms, therefore, an important aid to the advance of science, and a guarantee of its stability.

Summary.—The investigation of one of the most frequent and conspicuous chemical phenomena, *combustion,* showed that this consists in the interaction of the burning substances with a portion of the air. The substance constituting this portion is called oxygen, and the interaction takes place in such a way that the oxygen unites with the burning substances, forming with them new substances which together weigh more than the combustible substances had before weighed. The increase of weight is, in accordance with the law of the conservation of weight, equal to the weight of the oxygen which has at the same time disappeared.

Oxygen can be prepared in the pure condition by heating certain substances, *e.g.* oxide of mercury. It is found to be a colourless gas in which combustible substances burn more vigorously than in ordinary air.

Besides oxygen, metallic mercury is at the same time produced from the oxide of mercury. The weight of this and the oxygen is equal to the weight of the oxide of mercury which has disappeared. Mercury and oxygen are called the *constituents* of oxide of mercury, and the latter is called a *compound* of the two former.

The formation of compounds from their constituents takes place in *definite proportions by weight*, which depend only on the nature of the substances, and not on the circumstances under which the compounds are produced. *This law of constant proportions by weight holds for all kinds of chemical transformation whatever.*

The exactitude of this law is of the same order as that of the law of conservation of weight in chemical processes, *i.e.* no deviations from it have as yet been proved.

CHAPTER IV

THE CHEMICAL ELEMENTS

Elements and Compounds.—By the agency of heat we had succeeded in transforming oxide of mercury into more "simple" constituents, *i.e.* into substances whose *separate* weights are less than the weight of the original substance, while the *sum* of their weights is equal to the weight of the original substance. Similar "decompositions" can be effected by the application of other forms of energy, *e.g.* electrical energy. Imagine, now, all substances tested in this respect, and the "simpler" substances thereby obtained likewise subjected to the decomposition treatment. Substances will then be ultimately obtained which can in no way be decomposed into simpler ones, *i.e.* substances which in all chemical transformations can yield only substances of greater, or, at best, of equal weight.

Such substances are called *elements.* From what has just been said, it follows that the scientific conception of a chemical element is by no means that of a substance which is, in principle, "*undecomposable,*" but simply that of a substance which has hitherto never been converted into one of less mass than itself.

Despite the exceedingly large number of chemically different substances, amounting to many thousands, the number of the chemical elements is not great. There are, in all, seventy to eighty different substances into which all naturally occurring substances can be transformed, or of which they "consist." And, in fact, it has been found that the number of different elements into which a given substance can be separated is generally very small. By far the larger number of substances contain only two, three, or four elements; substances with a larger number of elements are comparatively rare.

The names of the elements so far known with certainty are as follows:—

Table of the Elements

Aluminium
Antimony
Argon
Arsenic
Barium
Beryllium

TABLE OF THE ELEMENTS—*Continued*

Bismuth
Boron
Bromine
Cadmium
Caesium
Calcium
Carbon
Cerium
Chlorine
Chromium
Cobalt
Copper
Erbium
Fluorine
Gadolinium
Gallium
Germanium
Gold
Helium
Hydrogen
Indium
Iodine
Iridium
Iron

Krypton
Lanthanum
Lead
Lithium
Magnesium
Manganese
Mercury
Molybdenum
Neodymium
Neon
Nickel
Niobium
Nitrogen
Osmium
Oxygen
Palladium
Phosphorus
Platinum
Potassium
Praseodymium
Rhodium
Rubidium
Ruthenium

Samarium
Scandium
Selenium
Silver
Silicon
Sodium
Strontium
Sulphur
Tantalum
Tellurium
Thallium
Thorium
Thulium
Tin
Titanium
Tungsten
Uranium
Vanadium
Xenon
Ytterbium
Yttrium
Zinc
Zirconium

The Elements.—Substances which in chemical transformations can only increase in weight, or *elements*, occur to a small extent in nature; for the most part, however, they are artificially prepared, *i.e.* obtained from their compounds (p. 39). The ways in which this is carried out, will not be considered till later. For the purpose, however, of obtaining a first general view of those substances which are most important in chemistry, we shall give a preliminary account of the chief properties of the elements and of some of their compounds, especially so far as they are usually known to a beginner from his experiences in ordinary life.

Since the number of the elements exceeds seventy, a classification of this large total is necessary. This is carried out on the basis of greater or less similarity of the elements and their compounds. Since a more exact knowledge is necessary before this similarity can be judged, it is not possible to explain here the grounds for the classification used; they will be discussed at the conclusion of the work.

The elements are, first of all, grouped into *non-metals* and *metals*. While the latter, which form by far the larger number, possess the well-known, easily recognisable properties which are connected with the conception of a metal, and which we meet with, say, in the case of silver, iron, or lead, there is no such common character in the non-metals; on the contrary, they exhibit a large variety of different properties. The further subdivision of these two groups is carried out on the principle of similarity, *i.e.* in accordance with agreement in the properties of their derivatives or compounds. The single groups are generally named after specially well-known or characteristic elements belonging to them.

As to the best classification of the elements, there has been much discussion. Since we are not dealing here with a question to be answered by yes or no, but with the judging between different considerations of suitability, it is natural that no definite decision has been reached, as also that such a decision is not a matter of very great importance. Under all circumstances it is well to bear in mind that every such scheme is one-sided, certain similarities being more strongly emphasised than others, and that it is more to the interest of the learner to recognise the possibility of various classifications than to make his knowledge one-sided by the idea of an "absolutely" best arrangement. The following arrangement affords a general view of the elements.

I. NON-METALS

A. Hydrogen and the halogens.
B. The oxygen group.
C. The nitrogen group.
D. The carbon group.
E. The argon group.

II. METALS

F. Alkali metals.	Light metals.
G. Alkaline earth metals.	
H. Earth metals.	
I. The iron group.	Heavy metals.
J. The copper group.	
K. Other metals.	

The above grouping is by no means ideal, still it has the advantage of bringing together the most important natural groups of the elements.

The two divisions of the metals, the light and the heavy, are so formed that the first division contains the metals whose density does not exceed 4, while to the second division belong the metals with higher density. With this apparently rather external and arbitrary distinction, there are bound up important chemical differences, which form the real justification of the division.

We pass now to the characterisation of the individual elements.

Non-Metals

A. HYDROGEN AND THE HALOGENS

Hydrogen is a colourless gas which is more difficult to bring into the liquid and solid state than any other substance.[1] It is the lightest of all known substances, for 1 cc. of it weighs under "normal" conditions, *i.e.* at 0° C. and under a pressure of 76 cm. mercury, only 0·000090 gm. It does not occur in appreciable quantity in nature, although there is probably a very small quantity of it present in the air.

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[1] Helium (p. 51) approaches very nearly and is even perhaps superior to hydrogen in this respect.

In compounds, hydrogen is met with very frequently. Water, which covers $\frac{4}{5}$ths of the earth's surface, is a compound of hydrogen with oxygen. Moreover, hydrogen is present in almost all the substances of which the bodies of animals and plants are built up.

Fluorine is a faintly yellowish-green coloured gas which does not occur in nature and which can be prepared only with difficulty, since it at once interacts chemically with almost all substances.

Its naturally occurring compounds are not rare; the best known is *fluorspar.*

Chlorine, likewise, does not occur free in nature, and must be prepared from its compounds. It is a yellow-green coloured gas with a powerful smell, and has a very harmful action on life of all kinds. By moderate pressure, it can be condensed to a yellow-green coloured, oily liquid, which is prepared on a manufacturing scale and sold in metal bottles. Chlorine, also, has the power of readily forming chemical compounds.

Compounds of chlorine occur widely in nature. The most important and best known is *common salt*, the familiar white substance, which is soluble in water and which we are wont to add to almost all our food.

Hydrochloric acid is a compound of chlorine and hydrogen.

Bromine is a dark brown-red liquid, transparent only in quite thin layers, and is one of the few elements which are liquid at ordinary temperatures. Even at room temperature, it passes very readily into a yellow-red, heavy vapour which has an exceedingly disagreeable smell and has a caustic action on all organisms. It shares with fluorine and chlorine the widely extended combining power, but possesses this to a less degree than those elements. Bromine does not occur free in nature.

The best known compound of bromine is *potassium bromide*, a white salt, readily soluble in water, which finds application in medicine and in photography. The bromine compounds occur, indeed, widely distributed in nature but generally in small quantities, so that bromine belongs to the somewhat rarer elements.

Iodine is a solid, crystalline substance of a blackish-violet colour, and with a lustre which approaches that of the metals. It volatilises slightly at room temperature; sufficient, however, for it to have a distinct and not pleasant smell. At higher temperatures it melts and passes into a vapour of a fine violet colour.

Iodine dissolves in various liquids, giving solutions which are sometimes coloured brown, sometimes violet. A solution of iodine in alcohol is employed in medicine under the name of tincture of iodine. It is a brown liquid having the smell of its two components.

Iodine does not occur free in nature; its compounds are sparsely distributed. *Potassium iodide*, a white salt readily becoming yellow or brown coloured owing to the separation of iodine, finds frequent application.

B. The Oxygen Group

Oxygen is a gas which forms a constituent of the atmospheric air (about $\frac{1}{5}$th), and as such is exceedingly important for living nature. The work or energy which the organisms require for the exercise of their functions, is derived from the combination of the substances of which they consist with oxygen. Likewise, all phenomena of combustion by means of which we warm our houses and drive our machines depend on the co-operation of oxygen.

Oxygen gas is, in thin layers, colourless; in very thick ones, blue. By strong cooling it can be condensed to a bluish liquid which boils at $-180°$ C.

Besides the large quantities of oxygen which occur free in the air there are also enormous quantities of the element contained in compounds. Most of the compound substances which we find at the earth's surface contain oxygen. Of these compounds, the most important is water (cf. p. 46). In weight, oxygen far surpasses all other elements at the earth's surface.

On account of the great importance of oxygen and of its compounds for all life, and on account of the very numerous compounds which it forms, this element occupies a specially prominent place in chemistry, and may be designated as the most important of all the elements.

Sulphur is a well-known, yellow, solid substance which melts at 120° C. to a honey-coloured liquid and readily inflames in the air. It burns with a blue flame, forming a gaseous oxygen compound which is easily recognised by its pungent odour.

Sulphur does not conduct electricity, and readily becomes negatively electrified on being rubbed.

Sulphur is widely distributed in nature. It occurs in large quantities, especially in volcanic regions, sometimes pure, sometimes impure through admixture with earthy matter. Not inconsiderable quantities of sulphur are also found in places where a decomposition of salts containing sulphur is effected by peat or brown coal.

Sulphur is met with in much larger quantity in chemical compounds than in the free state. *Gypsum* and *iron pyrites* may be mentioned as the best known of these substances.

Besides the oxygen compound of sulphur just mentioned, a hydrogen compound forces itself on the observation through its conspicuous and unpleasant smell. This substance is produced in the decomposition of many animal substances, *e.g.* eggs, and the "smell of rotten eggs" thereby produced is in reality the smell of the compound of sulphur and hydrogen, sulphuretted hydrogen.

Selenium and *Tellurium* are two very rare elements whose compounds are similar to those of sulphur, whereas the free elements differ in their properties. Selenium is generally a black-red, solid substance which does not conduct electricity. Besides this, however, another form of selenium is known which has a half-metallic lustre and a slight electrical conductivity. In nature, selenium occurs almost entirely in the form of compounds; occasionally, it is found in traces accompanying sulphur.

Tellurium is a grey, solid substance with metallic lustre, and conducts electricity like a metal. It, also, occurs in nature generally in compounds.

C. THE NITROGEN GROUP

Nitrogen is a gaseous element occurring, to a preponderating extent, in the free state; the amount of the nitrogen compounds, compared with that of elementary nitrogen in nature, is small. It forms the chief constituent of atmospheric air, which is a mixture (not a chemical compound) of $\frac{4}{5}$ths nitrogen and $\frac{1}{5}$th oxygen by volume. As can be understood from the known properties of the air, nitrogen is colourless, odourless, and tasteless. By great cold it, also, can be condensed to a liquid; with greater difficulty, however, than oxygen. Its boiling point lies lower than that of oxygen, viz., $-194°$ C.

Although the nitrogen compounds are, in amount, inferior to the free nitrogen, they are, nevertheless, of very great importance, since the most important constituents of the vegetable and animal structures are nitrogen compounds. Especially the substance of the muscles and the contents of the cells, the so-called protoplasm, to which the real life activity is attached, are nitrogenous.

Of the better known compounds of nitrogen in the mineral kingdom, *saltpetre* and *sal ammoniac* may be mentioned.

In contradistinction to the elements we have hitherto mentioned, elementary nitrogen possesses only in a very slight degree the power of interacting chemically with other substances. It is, therefore, characterised as a chemically inert or indifferent element. To obtain nitrogen compounds one cannot, therefore, as a rule, start from nitrogen itself, but the desired substance must be prepared from other nitrogen compounds.

Phosphorus is an element which is classed along with nitrogen, not on account of their similarity in the elementary state, but because of the similarity of the corresponding compounds. The free elements themselves are widely different.

Phosphorus is known in two different forms, which possess quite different properties but represent chemically, both of them, elementary phosphorus. This is seen from the fact that both forms, in their interaction with other substances, always give the same compounds in the same proportions, and each can be converted into the other without residue. The difference between them must be interpreted in somewhat the same way as the difference between water and ice, only that in the case of phosphorus the transformation does not take place so easily.

The first form of phosphorus is a semi-transparent, faintly yellowish substance which has the property of appearing luminous in moist air; it thereby evolves fumes and changes into an acid liquid. This is due to the fact that phosphorus, even at the ordinary temperature, combines with oxygen; it undergoes slow combustion. At a somewhat higher temperature, the slow combustion passes into rapid combustion, whereby the phosphorus burns with a bright, yellowish-white flame, with formation of white fumes.

The second form of phosphorus appears as a black-red powder which neither fumes nor appears luminous in the air, nor becomes visibly oxidised. This *red phosphorus*, also, takes fire much less easily than the first mentioned *white phosphorus*; having once taken fire, however, it burns in the same way as the white form.

Each variety can be transformed into the other by the action of heat. The relations which are here met with will be discussed later (Chap. XV.).

Only compounds of phosphorus occur in nature. These also play an important part in living nature. The bones of the vertebrate animals contain compounds of phosphorus, and serve as the starting-point for obtaining the element.

Arsenic, in its compounds, is closely allied to phosphorus, and in the free state, also, has a certain similarity to it. It is a black substance with a feeble metallic lustre, and conducts electricity like a metal. On being heated, it passes into a vapour without previously melting; the vapour, likewise, on cooling, passes directly into solid arsenic.

In nature, arsenic occurs both in the elementary state and in compounds, especially with the heavy metals.

The most conspicuous property of arsenic is its great poisonousness. All compounds of this element are more or less poisonous. Most of the cases of arsenical poisoning occur with an oxygen compound of this element, which is commonly called *white arsenic* or simply arsenic; it is a white, almost tasteless powder, slightly soluble in water.

D. THE CARBON GROUP

Carbon.—The peculiarity which was found in the case of some of the preceding elements, that there exist different solid forms which yield exactly the same transformation products, is present in a very marked degree in the case of carbon, for this element is known in three quite distinct forms. Ordinary black charcoal, the purest form of which is soot; graphite, the material of lead pencils; and, lastly, the diamond, the colourless, strongly refracting and exceedingly hard precious stone, all consist of carbon, and yield, in all chemical transformations, equal quantities of the same final product.

Besides these forms of elementary carbon, which generally occur in nature mixed with impurities, there are numerous compounds or derivatives of carbon. It is present in enormous quantities in the mineral world (in limestone), and forms a never absent constituent of all *organisms*. The different compounds of carbon occurring in the animal and vegetable kingdoms give rise, in chemical actions, to numerous other compounds. Above all other elements, carbon is endowed with the greatest power of forming different derivatives, and the number of substances which contain carbon so greatly exceeds the number of the compounds of the other elements that the chemistry of the carbon compounds forms, under the name of *organic chemistry*, a special part, and, indeed, as regards the number of known substances, the larger part of all chemistry.

These *organic compounds* consist, in the simplest cases, of carbon and hydrogen; to them belongs petroleum, which is a mixture of various "hydrocarbons" of similar composition and properties. Oxygen, in addition, is contained in the substances which are classed together under the name of the *fats*, and also in the starch and sugar-like substances which occur to a specially large extent in plants. The albuminoids, of which the muscles and the nerves are built up, and in which the chemical processes of life for the greater part take place, contain, besides the already-mentioned elements, nitrogen and generally also sulphur and phosphorus. That carbon is contained in all these substances is readily seen when they are strongly heated. The "charring" which thereby takes place, consists essentially in the other elements escaping as volatile compounds, leaving behind the portion of the carbon which does not disappear with these compounds, as charcoal.

After oxygen, carbon must be designated as the most important element.

Silicon is an element which does not occur in the free state on the earth. In the form of an oxygen compound, known as *silicic acid*, and of derivatives of this, silicon is, however, one of the most widely distributed elements.

Silicon, like carbon, can be obtained in various forms, as a brown powder, and as an iron-grey brittle mass with metallic lustre. This latter form conducts electricity.

An oxygen compound of silicon, silicic acid, constitutes, as quartz, a large part of the soil and the mountains. Compounds of silicic acid with various metals, especially of the group of light metals, compose most of the rocks. Silicon is, therefore, essentially the element of the solid crust of the earth.

Boron is an element which does not occur to a large extent in nature. It is never found free, but must be prepared from its compounds. The properties of elementary boron are similar to those of silicon.

The most important compound of boron is likewise that with oxygen. This is contained in *borax*, a salt used in the arts for soldering and for some other purposes, and which is the best known of all the compounds of boron.

E. The Argon Group

In atmospheric air, there are found in very small quantities a few gases which have only recently been discovered, and which are distinguished by the peculiarity that none of them has ever been changed into the compound state. They are known, therefore, only in the elementary state.

The longest known is *argon*, which is present in the air to the extent of rather more than $\frac{1}{100}$th part by weight, and remains behind when the other components have been converted into stable chemical compounds. It is a colourless gas, which, on account of its inability to form chemical compounds, is also odourless and tasteless. Its density is greater than that of air.

Besides argon, a few other gases of similar chemical indifference have been discovered. These, likewise, occur in the air, but in much smaller quantity; they are also contained in measurable quantity enclosed in some minerals. They are called *Helium*, *Neon*, *Krypton*, and *Xenon*.

The Light Metals

F. The Metals of the Alkali Group

The metals of this group have many properties in common. They have a low density, some of them lower than that of water. Their power of forming chemical compounds is very highly developed, so that they never occur free in nature, but must first be prepared by energetic means from their compounds. By reason of their great combining power they have the property of reacting chemically with most other substances, and can, therefore, be preserved only by observing special precautions.

Potassium.—Fresh surfaces of this light metal show a fine silver lustre. It readily melts, and is, even at room temperature, soft like wax. At a red heat it passes into vapour.

In nature, only compounds of potassium occur. As the best known of these, *saltpetre* and *potashes* may be cited. The most important is *carnallite*, which is obtained in large quantities in some parts of Germany, apparently as the residue left on the evaporation of a previously existent sea. Plants require potassium compounds for their growth, and where these are not present in the soil they are added as manure in the form of carnallite, or of the compound prepared from it and richer in potassium, potassium chloride.

Potassium compounds of all kinds play an important part in the arts and manufactures. Potassium is also of importance in the organism of man and the animals; it forms an essential component of the red blood corpuscles.

The elements *rubidium* and *caesium* are allied to potassium. Their properties are almost identical with those of potassium, both as elements and in compounds. In contrast with potassium, however, they occur in very small amount in nature.

Sodium is, in its properties, very similar to potassium. Its compounds are likewise found in enormous quantities in nature. The best known and most important of these is *common salt* (p. 46), which consists of sodium and chlorine. It serves as starting-point for the preparation of most of the other sodium compounds, as also of the chlorine compounds. *Soda* and *Glauber's salt* are also compounds of sodium.

Lithium is a rare element, which, in its properties and compounds, agrees least with the other elements of this group. It finds no great application.

G. The Alkaline Earth Metals

The elements of this group share with the alkali metals the property of a low density and of a highly developed combining power. Whereas these, however, cannot be exposed to the air without at once combining with the oxygen, the alkaline earth metals in a dry state remain unchanged in the air. They are also much more tenacious and more difficult to melt and to volatilise than the alkali metals; they have, therefore, more the character of the ordinary metals.

Magnesium is a white metal, somewhat of the colour of tin, which remains unchanged in the air as long as the temperature is low. On being heated it takes fire and burns with a brilliant light, forming an oxygen compound.

Compounds of magnesium occur very largely in nature. Almost all rocks which contain silicic acid also contain magnesium in the form of a compound with silicic acid. There are also other minerals which contain magnesium. In daily life several magnesium compounds find application; the most important are *magnesia*, which is an oxygen compound of the metal, and *Epsom salts*.

Metallic magnesium does not occur in nature any more than any of the other light metals.

Calcium in the free state is little known. Compounds of this element occur in nature in large quantities, and have an essential share in the building up of the earth's crust.

Of such compounds there should be mentioned *limestone* and *dolomite;* the latter contains magnesium as well as calcium.

Marble, the use of which is known, is a specially pure form of limestone. From limestone mortar is prepared. Gypsum, also, and cement, which find a similar application to mortar, contain calcium. The calcium compounds are largely applied in the manufactures.

Strontium and *barium* are two elements which, in their whole behaviour, are closely allied to calcium. Their compounds, however, occur in much smaller quantity, although they cannot actually be designated as rare.

Lastly, *beryllium* must be mentioned as an element belonging to this group. It has the same relation to the other members as lithium has to the other alkali metals, *i.e.* it shows less similarity to the other members than these to one another. It is a rare element, deriving its name from its occurrence in the mineral beryl.

H. The Earth Metals

The elements of this group have the character of the ordinary metals in a much more pronounced manner than those of the preceding groups. Of the large number of metals which could be mentioned here, only one, *aluminium*, can claim our attention, since the compounds of the others occur so rarely in nature that they play no important part, either with regard to the composition of the solid crust of the earth, or through application in the arts or in medicine.

Aluminium, which does not occur free in nature, is, in its oxygen compound and derivatives of it, widely distributed, and is, after oxygen and silicon, the third most frequent element in the earth's crust. It is an almost unfailing constituent of the rocks which contain silicic acid. When these undergo mechanical and chemical disintegration under the action of moisture and other atmospheric influences, *clay* separates out, which is a compound containing silicon and aluminium along with oxygen, and which, in different forms, is a chief constituent of the sedimentary or stratified rocks. The technical application of clay to the making of bricks, vessels, and modelled objects of all kinds is also very important.

For some years the metal aluminium has been prepared in large quantities from its compounds with the aid of the electric current. It is, as is known, a white, light metal which keeps well in dry air but is readily attacked in water, especially in salt water.

The remaining very rare alkaline earth metals we shall not describe here. The best known are *scandium*, *yttrium*, *lanthanum*, *cerium*, *neodymium*, *praseodymium*, *ytterbium*.

The Heavy Metals

I. Metals of the Iron Group

Iron is an element the properties of which, on account of its universal use, are well known. It is a hard, difficultly fusible metal which remains unchanged in perfectly dry air but in moist air, and under the influence of various substances, very quickly rusts, *i.e.* forms a compound with the oxygen of the air.

The somewhat different properties which iron exhibits as cast-iron, wrought-iron, and steel, are due to the presence of small amounts of other substances, of which carbon plays the most important part. The properties of pure iron agree most nearly with those of wrought and ingot iron, which are the purest commercial kinds of iron.

In nature, the occurrence of iron in the elementary state is exceptional; its compounds, however, are universally distributed and occur in large quantities. On the whole, iron occurs less frequently than aluminium but more frequently than calcium and magnesium.

Although iron compounds are present only in small amount in the animal and vegetable organism, they appear, nevertheless, to play a very important part, since the red blood corpuscles of the vertebrate animals, as well as the green substance of assimilating plants, contain iron.

Allied to iron are the nearly related elements *manganese*, *cobalt*, and *nickel*. They all belong to the less frequent, although not rare, elements.

Manganese, in the metallic state, greatly resembles iron, only that it rusts still more easily than the latter, thereby becoming coated with a black-brown oxygen compound. In the metallic state it is not much used. Its compound with oxygen, pyrolusite, however, which is employed for the production of a colour for pottery, has a varied and important application in the arts.

Cobalt is, even in moist air, much more resistant than iron and manganese, but finds little application as a metal. Its most remarkable property is that its oxygen compound dissolves in glass with a dark blue colour. It finds application, therefore, for the production of a blue colour, cobalt blue or smalt, and also for the colouring of glass and pottery.

Nickel is still less changeable in the air than cobalt and is, therefore, used for making articles intended to resist heat and moisture. Objects made of other metals are also, with the help of the electric current, plated with nickel; these nickel-plated articles preserve for a very long time the silver-like lustre of that metal, since nickel is also fairly hard and tenacious. In this fact lies the importance of this element as regards its applications. Nickel *compounds* are of no great importance.

Nickel mixed with copper and zinc forms German silver.

Chromium is a metal very similar to iron, only harder and more brittle, which remains quite unchanged in the air but is easily attacked by a number of liquids. The pure metal has no application; addition of chromium to steel improves the steel.

In nature it occurs chiefly in the form of an oxygen compound which also contains iron, and is called *chrome ironstone*.

It forms various compounds, of which *chromic acid* and *potassium chromate* have a varied application in the arts. The artists' colours also, chrome yellow and chrome red, are derivatives of chromic acid.

Allied to chromium in their chemical relations are several metallic elements of rare occurrence and possessing no great importance; it will be sufficient at this point to give their names. They are *molybdenum*, *tungsten*, *uranium*.

The two metals *zinc* and *cadmium* are, in many respects, related to the metals of the iron group, but show, on the other hand, a certain similarity to magnesium.

Zinc is a well-known grey-white metal, rather more resistant to the air than iron, but inferior to this in difficult fusibility and mechanical tenacity. As it can be readily rolled to sheets and soldered, it is applied for all purposes for which a not very tough metal, but one which is fairly resistant to water, can be used in sheet form.

In nature, zinc occurs only in the form of compounds, of which that with sulphur, called *zinc blende*, is the most important.

Cadmium is a metal which is very similar to zinc, only softer and more easily fusible, and which occurs in small amount along with zinc in its naturally occurring compounds or ores. The artists' colour, cadmium yellow or, shortly, cadmium, is the sulphur compound of the metal.

J. METALS OF THE COPPER GROUP

The metals here grouped together are distinguished from the preceding ones by a greater resistance to the chemical influences of air and water. This is, certainly, no perfectly universal characteristic, for while some of the members of this group belong to the noble metals which, under ordinary circumstances, do not change at all, others become more or less quickly coated in moist air with layers of oxygen compounds which destroy their metallic lustre. The action is, however, usually restricted to the surface, so that, after all, a fairly great durability with respect to the destructive chemical influences is present.

Connected directly with this property is the fact that these metals can be more readily obtained from their naturally occurring compounds or ores, than those previously mentioned, and also that they are often found in the free state. In this and the next group, therefore, the metals first met with in the history of the arts are found, and the metal mentioned in the oldest literary monuments and usually rendered in English by "bronze," is a mixture, the chief constituent of which is copper, the typical element of this group.

Copper is a metal which has been long known and whose red colour is found in no other metal. The true colour of copper is seen only on fresh surfaces, since it quickly tarnishes in the air, and becomes covered with a coating of oxygen and sulphur compounds which, however, is very thin and attains to no great thickness even after many years.

Copper is an excellent conductor of electricity and is, therefore, used for all kinds of electric conductors. Its chemical resistibility, combined with its toughness and high melting point, give it a wider technical applicability.

In nature, metallic copper is not of rare occurrence; of much more frequent occurrence, however, are its compounds with sulphur and oxygen.

Of the better-known compounds of copper, *copper vitriol*, a blue, crystalline salt, may be mentioned.

Lead is a grey, soft metal of high density and low melting-point. Its fresh surfaces exhibit a high metallic lustre; they tarnish, however, very readily through taking up oxygen from the air. The coating remains thin and the lead, therefore, resists further destruction for a very long time. It shows a similar behaviour with respect to many other attacks, so that it is indispensable in chemical manufactories in which corrosive substances are prepared.

On account of its great softness, pure lead is not much used. By alloying it with other metals it can be made harder, without its losing its chemical resistibility. It is also used for coating other metals, especially iron.

In nature lead occurs chiefly in the form of a sulphur compound, which is called *galena*, and is the most important lead ore.

Lead compounds are largely used in the arts. *Litharge* is an oxygen compound; *sugar of lead* a compound with acetic acid.

The lead compounds act on organisms as cumulative poisons. *i.e.* the effects of small amounts, which singly are not appreciable, are added and ultimately produce very serious symptoms.

Closely related to lead in many respects is the rare metal *thallium*, which, in other respects, is allied to the alkali metals.

Mercury is a metal, liquid at ordinary temperatures, which solidifies at − 39° C. and boils at + 357° C. It belongs to the noble metals, since it preserves its bright surface in moist air, *i.e.* it does not combine with the oxygen. At a higher temperature, however, combination takes place (p. 39).

Being the only metal which is liquid at ordinary temperatures, it is widely employed for physical apparatus, such as thermometers and barometers, and for other purposes in technical science. Its utility is greatly enhanced by its unchangeableness in air; its high density, also, is useful for some purposes.

In nature it occurs in the free state, but chiefly as a sulphur compound. This is called *cinnabar*; the artists' colour of the same name[1] is specially pure sulphide of mercury, which is usually artificially prepared.

The soluble mercury compounds act as powerful poisons; they have a wide application in medicine.

Silver is a white metal which remains unchanged in moist air. The brownish stain which silver objects sometimes exhibit is due to the formation of a silver compound through the action of air containing sulphur, or of other sulphurous substances.

On account of its comparatively rare occurrence, silver belongs to the more precious metals; on this and on its unchangeableness in air, depends its widespread employment as a metal for coinage.

In nature, silver occurs partly in the metallic state and partly as compounds with sulphur and arsenic.

Silver compounds are largely applied in photography, since many of them have the property of altering in light, and may, therefore, be used for the production of photographs. For this purpose, the compounds with the halogens, chlorine, bromine, and iodine are chiefly used.

Silver compounds are poisons for the organism. *Lunar caustic* is a soluble salt, the cauterising action of which is made use of in medicine. The turning black of the parts treated with caustic, depends on the alteration in light of the silver compounds produced. In the laboratory the solution is used as a reagent for the halogens.

K. The other Metals

The somewhat unsystematic classing together into one group of the metals not treated in the preceding groups, is, for the purpose of a first general view, justified by the fact that the number of more important and better known metals which have to be considered here is not large. A more detailed classification depending on the chemical relations, will be given towards the end of the work.

These last metals fall into two natural sub-groups, the one of which comprises the base metals, *i.e.* metals which undergo chemical change in air, the other, the noble metals. To the former belong *antimony*, *bismuth*, and *tin*, and to the latter *gold*, *platinum*, and the allied metals. To the former sub-group several other metals must also be added, which, on account of their rarity and small importance, do not call for a description at this point, which, however, we shall mention for the sake of completeness.

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[1] The pigment is also called vermilion in English.—Tr.

Antimony is a white, brittle metal, which melts at a red heat and remains practically unchanged in air. When heated, it burns fairly readily, forming an oxygen compound which is yellow when hot, white when cold.

In nature, it occurs chiefly in the form of a sulphur compound which is of a grey colour, has a metallic lustre, and is known as *antimony glance.*

Pure metallic antimony is not applied technically. Mixed with lead, it gives hard lead (p. 56) and type metal.

Various antimony compounds are used in medicine on account of their emetic action. The best known is *tartar emetic*, a salt of complex composition.

By reason of its general chemical relations, antimony should have been classed along with arsenic, to which it is in many respects closely related. The metallic nature, however, is so pronounced in the case of antimony and of bismuth, which is allied to antimony, that it appeared more suitable to group both together at this point.

Bismuth is a white, slightly reddish coloured, brittle metal, which, like antimony, remains lustrous under ordinary conditions and combines with the oxygen of the air only at comparatively high temperatures. It is fairly readily fusible.

In nature, bismuth occurs in the metallic state; it is also found in union with sulphur.

Bismuth finds application in the form of various metallic mixtures or alloys; some of its compounds are also used for medicinal purposes.

Several rare metals, which can only be named here, have to be classed along with antimony and bismuth. These are *vanadium*, *niobium*, *tantalum*. The somewhat more distantly related metals *gallium* and *indium*, may also be mentioned here.

Tin is a metal known from ancient times. It has a white colour, a fairly high degree of stability to water and air, and is readily fusible.

It is found in nature almost entirely in the form of an oxygen compound, *tinstone*, from which it can be readily obtained by fusion with charcoal. The ease with which it is obtained, explains why it became known so early.

Tin is applied in the metallic state to the manufacture of utensils, tubes, etc., where its unalterability, especially in moisture, is essential. Other metals, such as iron and copper, are coated with tin to protect them from the formation of their oxygen compounds. In the former case it is done for the sake of durability, in the latter, to prevent the formation of poisonous compounds (for example, in kitchen utensils).

Tin is also used for many alloys; it is employed, mixed with mercury as tin amalgam, for coating mirrors.

Compounds of tin are chiefly used in dye-works and in chemical industries.

Allied to tin are several rather rare metals, which we shall mention here. They are *titanium*, *germanium*, *zirconium*, *thorium*. The oxide of the last forms the chief constituent of incandescent mantles.

Gold is a yellow, heavy metal, which does not alter in air, either when cold or when heated, and remains stable, also, to other chemical influences. It is re-obtained from its compounds by simply heating these, provided that the other constituents can volatilise. It may, therefore, be regarded as the type of the noble metals, *i.e.* metals not inclined to form chemical compounds.

Gold, accordingly, occurs in nature almost entirely in the metallic state, sometimes mixed or alloyed with other noble metals, especially silver.

The use of gold for ornaments and coinage is known. On account of its scarce occurrence, it has a high value; on account of its unalterability, it is suitable for money tokens.

Compounds of gold are obtained most readily by the aid of chlorine. They have no extended application.

Platinum is a grey, very difficultly fusible metal, which is similar to gold with respect to its combining power. It is used, therefore, in making chemical apparatus which have to resist high temperature and strong chemical influences. This property is made use of not only in the laboratory but also in the industries.

In nature, it occurs in the metallic state mixed with other metals which have similar properties. Since these, however, are still rarer than platinum, their application is exceptional. They are called *ruthenium*, *rhodium*, *palladium*, *osmium*, and *iridium*.

Historical.—The conception of an element is found as far back as Greek philosophy, although in an essentially different form and not in agreement with the facts. The most widespread view was that of Aristotle of the four elements, fire, air, water, and earth. The conception of these elements was not that all substances are composed of them, but rather that these were the representatives of the fundamental properties, which he had chosen as being moisture, dryness, heat, and cold.

During the slow development of chemical knowledge in the middle ages, it was seen that these properties had been very unsuitably chosen, and that there were other properties which were much more closely connected with the general behaviour of substances. Representatives of these properties were, therefore, looked for. Thus, the *metallic* properties were symbolised by *mercury*, *combustibility* by *sulphur*, *solubility in water* and the power of acting on the organ of taste by *salt*, and, lastly, *stability* to the action of water and fire by *earth*: these four substances were accordingly regarded as the elements. The formation of this conception also, is based on the view that the properties of indifferent "matter" represented by these elements could be, by suitable actions, withdrawn or communicated at will. The endeavour to artificially bestow the properties of the most valuable of all metals, gold, on metals of less value, and thus to make gold, was, accordingly, closely connected with these theoretical views.

Just as the negative results of all attempts to construct a *perpetuum mobile* led to the positive law of the conservation of energy, the negative results of the attempts to make gold have led to the positive law that the elements can be prepared only from their compounds, and never from other elements or their compounds, where the element in question is excluded. In other words, there also holds a *law of conservation of the elements*, to the effect that, by means of any chemical process carried out with definite amounts of definite elements, only these elements, in the original amount (or compounds of them in corresponding amount), can be re-obtained, but never other elements.

This law was not recognised at one definite time by one particular investigator, but has gradually been obtained as the result of general experience. It has arisen in connection with the development of the conception of an element as a ponderable constituent of substances (in the sense set forth on p. 43). Whereas the elements of antiquity and the middle ages were, essentially, the bearers of certain properties, the elements of the present day are the ultimate constituents in chemical analysis. The English chemist and physicist Robert Boyle (*c.* 1660), did substantial work towards the carrying through of this conception.

The work of characterising and of distinguishing between the different elements has been performed chiefly in the eighteenth and nineteenth centuries. At the beginning of the latter, especially, the English scientist Humphry Davy discovered the light metals, the oxides of which had formerly been regarded as elements from the fact that it was not known how to decompose them, and established the elementary nature of the halogens.

A very productive method for the discovery of new elements was found about the middle of the nineteenth century by the German chemist Robert Bunsen, who showed how the elements present could be recognised by the rays emitted by the glowing vapours of different substances. He himself immediately discovered, in this manner, two new elements, and since then almost all further discoveries in this department have been made by the aid of the method of "spectrum analysis."

CHAPTER V

OXYGEN

General.—With this chapter we commence the more detailed study of the separate elements and of their compounds with one another. In general, the arrangement will be such that in the case of each element its compounds with the elements previously discussed will be treated.

Along with the description of the nature of the *substances* the general *laws* of chemistry will be treated, and this will be done in such a way that each law will be discussed at the point where it first finds application. The attempt has been made to so arrange the whole subject-matter that both these tasks shall be performed without the one or the other thereby suffering.

In this treatment, also, laws and relations are considered which are usually discussed in physics. The reason of this is that a knowledge of these laws is of the greatest importance for the correct interpretation of chemical phenomena, and these things must, therefore, be given in such a form that the chemist can directly apply them.

Oxygen.—The discussions relating to the phenomena of combustion had led to a preliminary knowledge of oxygen as being an element playing an essential part in these phenomena (p. 36). The substance itself was characterised only so far as was necessary for the immediate purpose. We have here, now, the further task of developing the general knowledge of this substance beyond that single relation.

Production from Potassium Chlorate.—The preparation of oxygen from oxide of mercury was, as we saw, a process which required a fairly high temperature and at the same time, took place slowly. It is, therefore, desirable, if one would become more closely acquainted with the properties of oxygen, to possess a more richly flowing source of it. It is true that in the air there are enormous quantities of oxygen present; it is, however, not easy to free it from the other substances with which it is mixed.

In the substance known as *potassium chlorate* or *chlorate of potash*, which is used as a medicament and for the preparation of fire-works, inflammable material, and many other things, we have the sought-for source of pure oxygen.

By the same means by which we obtained it from oxide of mercury, viz., by heating, oxygen may also be obtained from potassium chlorate, and this in a much larger proportion and at a lower temperature. The evolution of oxygen takes place with especial readiness when the potassium chlorate is mixed with certain other substances; for this purpose the already mentioned mineral pyrolusite (p. 54) is very effective. This substance undergoes no change in the reaction.[1] The reason for its action will be given at a later point (Chap. XX.).

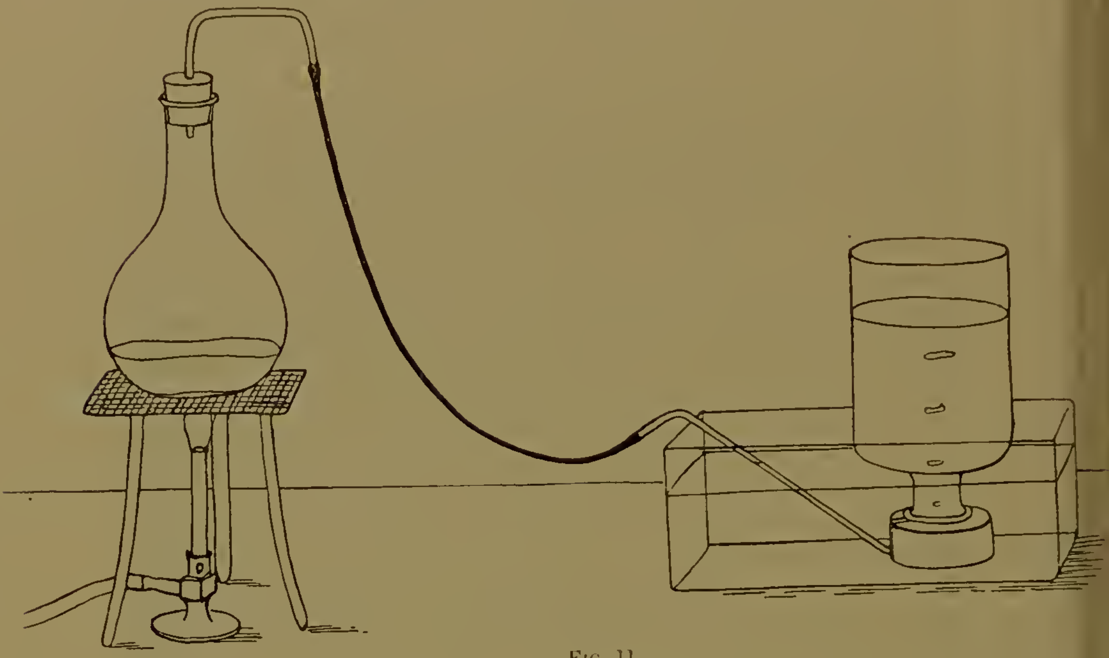

FIG. 11.

If, now, a mixture of potassium chlorate with one-fourth of its weight of pyrolusite be heated in a thin glass flask furnished with a delivery tube, we soon observe the evolution of a gas, and this occurs so rapidly that the flame must be removed from time to time in order that the flask may not be burst by the pressure of the too rapidly evolved gas. The gas is collected as before in bottles (Fig. 11).

Identification of Oxygen.—We must, first of all, convince ourselves that it is really with oxygen we are dealing. For this purpose we recall the fact that we had identified oxygen by the bursting into flame of a glowing chip of wood, which we brought into contact with the gas. We repeat the experiment with the gas obtained from potassium chlorate and observe the same phenomenon. A glowing wood-chip is a *reagent* for oxygen, and the *reaction* consists in its inflaming.

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[1] Pyrolusite, certainly, evolves oxygen on being heated, but none at the temperature at which potassium chlorate is decomposed.

Explanation of the Oxygen Reaction.—Since the combustion of wood in air takes place at the cost of the oxygen therein contained, the question must be asked why the phenomenon has such an essentially different aspect in pure oxygen from that in air. The answer is as follows:—

When the wood burns, a certain amount of heat is produced, which serves to heat the gaseous products of combustion, and the higher the temperature thereby rises, the brighter will be the light emitted and the more rapid will be the combustion. When, now, the combustion takes place in *air*, not only must the products of combustion be raised in temperature by the heat produced, but also the nitrogen which is contained along with the oxygen, in four times its amount, in the air. On account of the much greater amount of substance to be heated, the temperature does not rise so high in the case of combustions in air as in pure oxygen, and, therefore, the phenomena of combustion are much less energetic.

This result of our consideration, obtained deductively (p. 40), can be tested by mixing pure oxygen with other gases which neither are combustible nor support combustion; as a matter of fact, the vigorousness of the combustion becomes less in such a mixture, and if the proportion of oxygen in it is very small, no combustion at all can be brought about in it.

Combustion of other Substances.—It follows from the explanation just given that other substances also, which burn in air, will exhibit the phenomena of combustion much more vigorously in oxygen. And still further, one must expect that substances can exist which cannot be made to burn vigorously in air, because the requisite temperature is not reached, but which can burn vigorously in oxygen. Experience confirms both conclusions.

The first phenomenon is seen in the case of sulphur and phosphorus. Sulphur burns in air with a pale blue flame, scarcely visible in daylight. If, however, the burning sulphur be introduced on a long-stemmed iron spoon into a bottle of oxygen, it flares up vigorously and rapidly burns with a bright blue flame.

The difference is seen still more clearly with phosphorus. A piece of phosphorus placed in a similar spoon and ignited, burns in the air with a yellowish-white flame, similar to that of a candle. If the spoon be lowered into oxygen, the bottle forthwith becomes filled with a sun-bright light.

Combustion of Iron.—A substance which cannot be easily made to burn in air, is *iron*. When a piece of iron, a watch-spring for example, is heated in air, it certainly combines with the oxygen, and the compound produced coats the iron as a grey, brittle mass which breaks off on bending the iron. It does not, however, continue burning, and it is only when small particles of iron are scattered in the flame that they can be heated so as to burn entirely (p. 34).

The combustion of iron in oxygen, however, takes place much more readily. A thin steel watch-spring, to the end of which is attached a piece of touch-wood or tinder, can be burned in oxygen like wood. First, the glowing tinder bursts into a vigorous flame, whereby the end of the watch-spring becomes white-hot; then the iron begins to burn with scintillations, and the product of combustion falls down from time to time in the form of a white-hot slag. To prevent this cracking the glass, it is well to fill the bottle one-third full with water.

Oxides.—Almost all the chemical elements are capable of entering into combination with oxygen, and of forming new substances with corresponding increase of weight. From the Greek name for oxygen, *oxygenion*, its compounds with other elements (and also with some compound substances) are called *oxides*. Thus, oxide of mercury is, as we have already learned, a compound of mercury with oxygen. In nature, oxygen and its compounds have a very large distribution. From its occurrence in atmospheric air, which surrounds the whole surface of our earth and penetrates into all its interstices, it follows that those substances which can form compounds with oxygen at the ordinary temperature, must have done so to a large extent in the course of the centuries. This is one of the causes of the wide distribution of oxygen compounds in nature.

The Existence of Combustible Substances.—Combustible substances, *i.e.* substances capable of combining with oxygen, are, nevertheless, present in large amount in nature in the unburnt condition, and the question arises, why these have not been burned up long ago. Thus a piece of charcoal or of sulphur can lie exposed to the air for years, or indeed, for centuries, without apparently undergoing combustion. That this may take place, the sulphur must be ignited, and we have to ask what fresh circumstance is thereby introduced.

Igniting consists in heating one spot of the combustible body to a comparatively high temperature (somewhere about 500° to 600°). It is quite indifferent in what manner the heating is effected; the temperature and contact with oxygen are alone of importance. The heated part then begins to burn. An amount of heat is thereby set free by which the adjacent parts of the combustible substance, in their turn, are heated. Combustion passes over to these parts, and so the process goes on till all is burned.

The only point in which the burning portions are distinguished from those which are not burning, is their temperature. It seems as if most substances had the power of combining with oxygen only at comparatively high temperatures. This view would, however, not be quite a correct one. On making the appropriate investigation, no temperature can be found at which combustion just begins, and such that below this point, no combustion takes place at all. On the contrary, we are dealing here with a gradual transition.

Combustible substances, therefore, combine with oxygen at all temperatures, but *with very different velocities.* The higher the temperature, the more rapid is the combination; on the other hand, as the temperature falls, the process becomes slower and soon diminishes so as to be inappreciable.

* **Slow Combustion.**—A body can, accordingly, begin to combine with oxygen at certain middle temperatures, without taking fire. Ignition occurs only when the heat developed in the combustion raises the adjacent portions of the body to such a high temperature that these also burn with sufficient rapidity. The temperature which these adjacent parts attain, depends, on the one hand, on the amount of heat conveyed to them by the combustion, and, on the other hand, on the amount of heat which they lose by conduction and radiation. Not until the former exceeds the latter sufficiently to maintain the temperature of rapid combustion, can this rapid combustion take place. From this it follows that ignition or the initiation of an independent combustion, depends quite as much on the form and distribution of the substances as on their nature, as our every-day experience with regard to the ignition of combustible substances teaches us.

Influence of Temperature on the Velocity.—The law that the velocity of chemical processes, *i.e.* the ratio of the amount transformed to the time required, rapidly increases with rising temperature, is quite universal, and is valid for chemical processes of all kinds. We have, in general, no ground for supposing that any chemical process which takes place at a higher temperature, cannot take place at a lower. If we do not note any transformation, that is merely because it takes place too slowly for our observation.

The stock of coal in the cellar burns while it is stored in the cellar just as when it is in the fire; only, in the former case, with so great slowness that we can detect no difference even after several years. If large quantities of coal, however, are stored under such conditions that the dissipation of the heat developed in the slow combustion is prevented, the temperature rises, the process is accelerated, and can become so rapid that it passes into vigorous combustion. This phenomenon is called the spontaneous ignition of coal.

Physical Properties of Oxygen.—To determine the *density* of oxygen, one must determine the weight of a given amount and the volume occupied by it (p. 27). The latter can be easily done in a glass tube graduated in cubic centimetres. The weight is less easy to determine, as oxygen is very light, and the determination of its weight in the large vessels necessary causes difficulties. We adopt, therefore, an indirect method.

Potassium chlorate, as we know, evolves oxygen on being heated. In the vessel, a white substance remains behind; a further substance is not produced. If, therefore, the weight of the potassium chlorate taken for the experiment be determined, and, afterwards, the weight of the residue, the difference is equal to the weight of the oxygen evolved. If this is collected in a suitable measuring-vessel (Fig. 12), its volume can be read off and its density calculated by the formula $d = m/v$. If the experiment is performed with 1 gm. of potassium chlorate, it is found that after complete decomposition, the oxygen evolved, on cooling down to room temperature, occupies, in round numbers, 290 cc. The loss of weight of the potassium chlorate amounts to 0·392 gm., and the density of oxygen is, therefore, 0·00135.

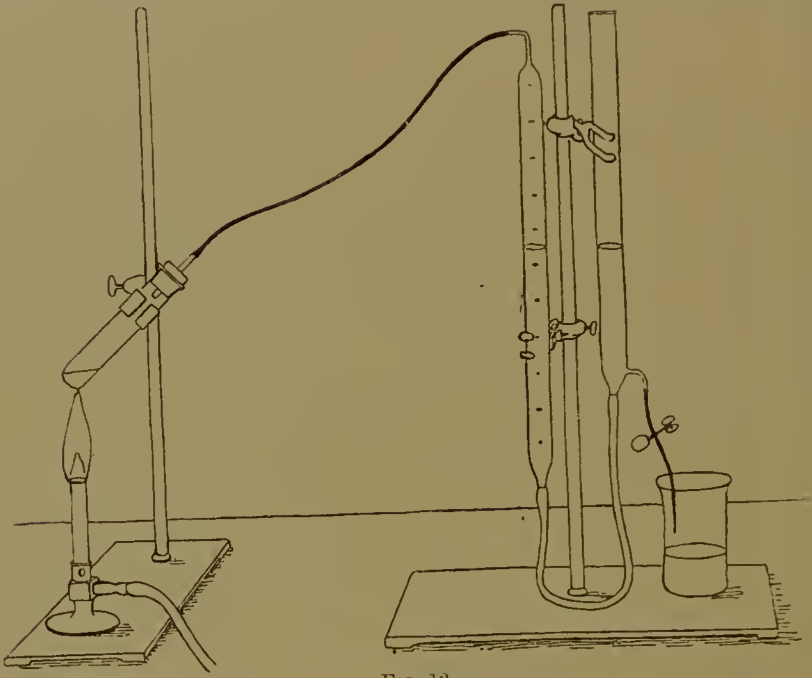

Fig. 12.

Normal Temperature and Normal Pressure.—This result is, however, not yet defined with sufficient exactness. The volume occupied by a gas depends, in large measure, on the pressure and temperature, and values for the density, varying within wide limits, will, therefore, be obtained when the determination is performed under different conditions. An agreement has, therefore, been come to with regard to a normal temperature and a normal pressure, at which the densities of gases shall be determined. As normal temperature the melting point of ice is taken; on the centigrade thermometers this point is marked 0°.[1]

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[1] In England, for the purposes of daily life, thermometers with the Fahrenheit scale are used. On this scale the melting point of ice is marked 32°. One degree on the Fahrenheit scale is equal to $\frac{5}{9}$ths of a degree on the centigrade scale.—Tr.

As normal pressure there has been adopted the mean atmospheric pressure, which is taken equal to the pressure of a column of mercury 76 cm. high.

Since, however, the density of mercury is also dependent on the temperature, we must add that the temperature of the mercury shall be 0° C. The density of mercury is then equal to 13·595; 1 cc. weighs, therefore, 13·595 gm., and a column of 1 sq. cm. section and 76 cm. high weighs 76 × 13·595 = 1033·2 gm.

The pressure of one atmosphere is, therefore, equal in effect to a weight of 1033 gm., or rather more than 1 kilogm., on a area of 1 sq. cm.[1]

Boyle's Law.—The volume occupied by oxygen gas cannot be always determined at 0° C. and under atmospheric pressure, and the determination made under other conditions must be appropriately reduced. For this purpose, a knowledge of the behaviour of oxygen to changes of pressure and temperature is necessary.

A knowledge of the first is obtained by means of the apparatus shown in Fig. 13. The oxygen is contained in a graduated tube, the lower end of which passes into an indiarubber tube; to the other end of this a movable vessel is attached. Part of the measuring tube, the indiarubber tube, and the vessel are filled with mercury. The pressure under which the oxygen stands can be altered by raising and lowering the vessel. The volume occupied by the oxygen can be read off on the graduated tube. The pressure in cm. of mercury, is the sum of the external atmospheric pressure (height of the barometer) and the difference of level of the two surfaces of mercury. This difference of level is to be reckoned with negative sign when the outer mercury surface stands lower than that which bounds the oxygen. A

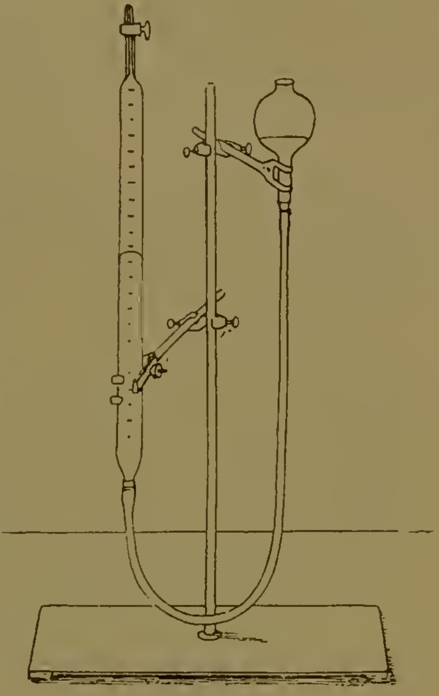

Fig. 13.

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[1] Since the weight of a given mass varies somewhat with the place, the unit of pressure defined above is also subject to the same variation. In cases of greater exactness it is assumed that the weight determination is made at sea-level and in the latitude of 45° or, that the determination, when made elsewhere, is recalculated to these conditions.

The adoption of *absolute units* is still better. Since the force with which 1 gram acts in consequence of gravitation, is, at sea-level and in latitude 45°, equal to 980·53 absolute units (p. 24), it follows that the pressure of the atmosphere is equal to 980·53 × 1033·2 = 1013130, or very nearly 10^6 absolute units. A column of mercury 75 instead of 76) cm. high would give, almost exactly, 10^6 absolute units of pressure.

number of corresponding values of volume and pressure are in this way determined.

By means of such measurements, which have been carried out by various physicists with great care, it has been found that a very simple relation exists between pressure and volume. Denoting any two pressures by p_1 and p_2, and the corresponding volumes of oxygen by v_1 and v_2, the formula holds, $p_1 : p_2 = v_2 : v_1$, or, $p_1v_1 = p_2v_2$. The pressures are, therefore, inversely proportional to the volumes, or the products of all corresponding values of pressure and volume are equal.

The law found here for oxygen gas is not peculiar to this substance, but holds equally for all other gases. It was discovered in 1660 by Boyle, and is called after him.

The Law of Gay-Lussac and Dalton.—Pressure is not the only circumstance which influences the volume of a gas. The volume changes also with the temperature, increasing and diminishing in the same sense as the temperature rises and falls. To determine the amount of this change it is necessary to choose another fixed temperature besides that of melting ice. The temperature of boiling water, and, since this changes with the pressure, the temperature of water boiling under a pressure of one atmosphere (= 76 cm. mercury) serves as such a temperature.

To obtain the amount of the change of volume between these two temperatures, we use the same apparatus as was employed in demonstrating Boyle's law (Fig. 14). The graduated tube containing the oxygen is surrounded with a glass mantle in which are placed water and pieces of ice. The oxygen soon assumes the temperature of melting ice, and, after the outer vessel has been so placed that the two mercury surfaces stand at an equal height, the volume occupied by the oxygen at 0° C. and under the then existing atmospheric pressure, can be read off.

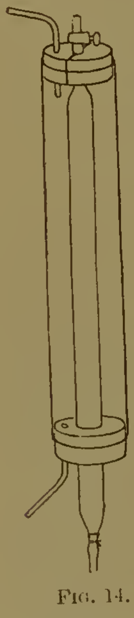

FIG. 14.

The ice is then removed, and in its place steam is passed through the mantle. The volume of the oxygen increases, and, having again brought the two mercury surfaces to the same height, we can read off the volume which the oxygen occupies under the same pressure as before, and at the temperature of boiling water. Exact measurements of the amount of change show that the volume has increased in the proportion 1 : 1·367.

This relation has also proved to be a universal law valid for all gases. The number obtained is, therefore, the expression not of a special property of oxygen but of a universal property of the gaseous state. The law, that all gases expand by the same amount between corresponding temperatures, was discovered simultaneously by Dalton and Gay-Lussac in the year 1801; it is generally called after the latter. In symbols, the law can be formulated thus:—

$$v_t = (1 + at)v_0,$$

here v_t is the volume at the temperature t, v_0 that at the melting oint of ice, and a the hundredth part of the expansion between the nelting point of ice (0° C.) and the boiling point of water (100° C.). n numbers, $a = 0·00367$ or 1/273.

This formula gives the expansion starting from the temperature of nelting ice. To obtain the expansion between any two temperatures and t', the above formula is applied to both temperatures, and v_0 liminated from the two equations. There is obtained

$$\frac{v_t}{1 + at} = \frac{v_{t'}}{1 + at'} = v_0.$$

From this it is seen that the volume observed at temperature t is educed to the volume at normal temperature, 0° C., by dividing it by he quantity $1 + at$.

* It must be specially emphasised that the quantity a is the hundredth part of the expansion of unit volume between the melting oint of ice and the boiling point of water, and not, let us say, between ny one temperature and another 100° C. higher. As can easily be seen, the value of a, the *coefficient of expansion of gases*, is dependent on he choice of the initial temperature.

The Temperature Scale.—Since the expansion by heat has the same value for all gases, independently of their nature, the change of olume of gases is used for temperature divisions. The temperature f melting ice is called zero and that of water boiling under atmospheric ressure 100. This range of temperature is divided into a hundred arts or *degrees*, which are proportional to the change of volume. To listinguish this graduation from others which are also used, it is called he centigrade or the Celsius scale, and is denoted by C.

Let, then, the volume of a given quantity of oxygen or of another gas contained in a tube, be denoted by 0° C. (Fig. 15), the volume at he boiling point of water will be defined by the spot marked 100° C., nd the volumes *oe* and *os* will be to one another as 1 : 1·367. The ength *es* is divided into one hundred parts, and each of these parts denotes ° C. Such a tube, in which the gas is enclosed by means of an easy-noving piston, and which is graduated in the manner just described, ould, evidently, be used as a thermometer or measurer of temperature.

The Absolute Zero.—The temperatures, however, which are met ith, are not confined to the range between the melting point of ice nd the boiling point. Beyond the latter, we can, evidently, extend ur thermometers indefinitely, for there is no evidence of a limit for igher temperatures.

Towards the other side, however, our thermometer is limited, for we an subtract only a definite number of degrees before reaching the ero point of volume. This number can be calculated as follows. If we take the volume $oe = 1$, the volume $es = 0·367$; one degree is the hundredth part of this; its volume, therefore, amounts to 0·00367, and we can subtract, in the direction of o, only as many degrees as the number of times this fraction is contained in the unit. Now, $1/0·00367 = 273$; if we could lower the temperature 273° below the melting point, the oxygen or any other gas must occupy the volume zero.

Apart from the fact that all gases liquefy before this condition is reached, such a low temperature has, as a matter of fact, never been produced; the lowest point which has been reached lies at 263° below the melting point of ice, and the increasing difficulties of descending lower make it quite probable that the point $-273°$ will never be reached. This point is called the absolute zero.

The Absolute Temperature.—The designation of the temperature of melting ice by 0° C. results in the temperatures below this having negative values. This is not only arbitrary, but, in a certain sense, inconsistent, since different temperatures never have the relation to one another of positive and negative magnitudes in the mathematical sense. In science, therefore, another method of reckoning the temperature has come into use. As zero there is taken that unattainable temperature 273° C. below the melting point of ice, and the temperature is counted from that point upwards, with the same degree divisions as in the centigrade scale.

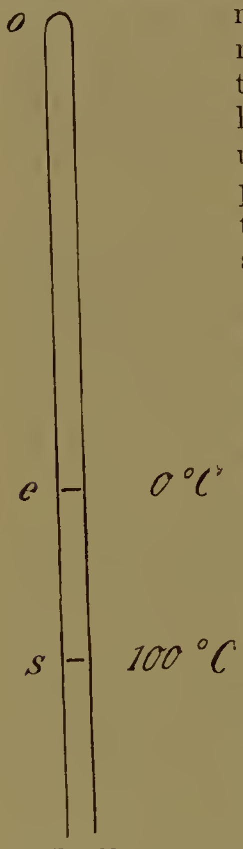

FIG. 15.

Besides the gain of entirely avoiding negative temperature numbers, there is the further advantage that with this method of reckoning, the law of expansion of gases assumes an especially simple form; the volume becomes simply proportional to the temperature. If the volume oe of our gas thermometer (Fig. 15) is divided into 273 parts, and if this graduation is continued upwards to any extent, the volume measured in these units gives directly the numerical value of the temperature. The temperature measured in this manner is called the *absolute temperature*, in contradistinction to the centigrade temperature reckoned from the melting point of ice. The relation between the two scales is very simple, for the absolute degrees amount to 273 units more than the centigrade degrees. If the former are denoted by T and the latter by t, we have the relation

$$T = 273 + t,$$

where, of course, negative centigrade temperatures must be reckoned with their sign, *i.e* must be subtracted from 273.

To distinguish the *numerical* values of the absolute from the centigrade temperatures, the former are designated by the letter A.; thus, n° A. = $(n - 273)^\circ$ C.

Simultaneous Validity of the Gas Laws.—In the previous discussions some assumptions have been tacitly made which shall now receive expression. Since the volume of a gas is influenced both by the temperature and the pressure, it must, of course, be assumed that the laws stated for the influence of these factors separately, viz., Boyle's law and Gay-Lussac's law, are valid only for the case that the other variable is kept constant. In other words, Boyle's law holds only when the temperature is constant, and Gay-Lussac's law only when the pressure is constant; the former, however, is valid at any constant temperature, and the latter at any constant pressure.

We will first answer the question, how great is the increase of pressure of a gas when we warm it without increasing its volume. Let us start from 0° C. and the pressure p_o, under which conditions let the gas occupy the volume v_o, and warm it at constant pressure to t°; the volume will then be, according to Gay-Lussac's law, $v_t = v_o(1 + at)$. To again obtain the former volume v_o, we must increase the pressure. The necessary value p_t is got from Boyle's law; since the pressures and volumes which go together are v_t and p_o, or v_o and p_t, we have $v_o p_t = v_t p_o$. Eliminating, by means of this, v_o (or v_t) from the former equation, there follows

$$p_t = p_o(1 + at).$$

That is, the increase of pressure caused by change of temperature at constant volume, takes place in the same proportion as the change of volume under constant pressure. Or, the coefficient of expansion of gases is equal to their coefficient of increase of pressure.

The General Gas Law.—In the case where the pressure and temperature are changed simultaneously, we arrive at the result by the following line of argument. When the temperature is the same, we have the relation $p_1 v_1 = p_2 v_2$ (p. 68). If the temperature is changed there holds, when the pressure is constant, $\frac{v_1}{1 + at_1} = \frac{v_2}{1 + at_2}$ (p. 69), and when the volume is constant, $\frac{p_1}{1 + at_1} = \frac{p_2}{1 + at_2}$ (*vide supra*). It is, therefore, a matter of indifference whether the influence of temperature be taken into account along with the pressure or with the volume; it is represented by the same formula in both cases. Accordingly, if pressure, temperature, and volume are simultaneously changed, there holds, universally, the equation

$$\frac{p_1 v_1}{1 + at_1} = \frac{p_2 v_2}{1 + at_2}.$$

From this we obtain the formula for the reduction of the volume of a gas observed at any temperature t and under any pressure p, to the volume v_o which the gas would occupy at the temperature $t_o = 0°$ C. and under the pressure $p_o = 76$ cm. mercury. For, since in accordance with the given formula, there must also hold the relation

$$\frac{pv}{1 + at} = \frac{p_o v_o}{1 + at_o},$$

there follows, on setting $t_o = 0$,

$$v_o = \frac{pv}{p_o(1 + at)},$$

a formula which is of frequent application.

The fact has still to be referred to that, according to the general formula, the quantity $\frac{pv}{1 + at}$ has always the same value for a given quantity of a gas, whatever the pressure, temperature, and volume of the gas may be. This relation is expressed by the formula $\frac{pv}{1 + at} = \text{const.}$ Of the three magnitudes p, v, t, therefore, only *two* can be taken as independent; when these are chosen the third is fixed.

By introducing the absolute temperature, the complete gas law becomes still clearer. From the equation $\frac{p_1 v_1}{1 + \alpha t_1} = \frac{p_2 v_2}{1 + \alpha t_2}$ or $\frac{p_1 v_1}{p_2 v_2} = \frac{1 + \alpha t_1}{1 + \alpha t_2}$, there is obtained, when we make $t_1 = T_1 - 273$, and $t_2 = T_2 - 273$, since $\alpha = 1/273$, $\frac{p_1 v_1}{p_2 v_2} = \frac{T_1}{T_2}$ or $\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2}$. The expression $\frac{pv}{T}$ remains constant, therefore, for all possible values which the temperature, pressure, and volume of a given quantity of a gas can assume. Denoting this constant, which is proportional to the quantity of the gas, by r, the general gas law reads

$$pv = rT.$$

The Number of Variables. Degrees of Freedom.—Lastly, we shall refer to still one point which, it is true, appears very "self-evident," which we shall, however, find later to be of great importance. The gas law contains three variable magnitudes—pressure, volume, and temperature. Of these, however, only two can be arbitrarily fixed; if values have been chosen for these, the equation can be satisfied only when the third assumes a quite definite value, which is obtained by substituting the two values in the equation, $pv = rT$. The importance of the gas law, indeed, lies just in the fact that it allows of calculating the third value from the other two. It is indifferent which two of the three variables are chosen as the magnitudes to be arbitrarily fixed.

This relation is expressed by saying, *the gaseous state has two degrees of freedom.*

For understanding the behaviour of different systems, a knowledge of their degrees of freedom is a matter of fundamental importance, and this is true not only for the physical, but also for the chemical behaviour. Much use will, therefore, be made later of the conception of the degrees of freedom of a system.

* **Geometrical Representation of the Gas Laws.**—It will be recalled that in Mathematics, the fact of the mutual dependence of two variable magnitudes, of such a kind that, one of them being given the other must assume a definite value, was expressed by saying that the one is a *function* of the other. In Boyle's law

$$pv = C,$$

where p is the pressure, v the volume of a gas, and C a constant, p is a function of v. Conversely, v is a function of p, for this relation is, necessarily, always mutual.

As can be seen from this example, the content of a quantitative law of nature can be expressed by saying that it represents two (or several) measurable properties of a system as functions of one another.

When the function is given in the form of an algebraic equation there can be calculated for each value of the one variable the corresponding value of the other, and when such calculations have to be frequently performed, a table of the required extent can, once for all, be drawn up. In many cases, however, especially in the investigation of new relations, an algebraic expression for a really existing dependence is not known. In such cases it is important to possess a method which allows of showing clearly the connection between the magnitudes, so that the general relations can be judged. For this purpose the representation by means of *co-ordinates* is generally used in the experimental sciences.

Let it have been found by measurement that to a definite value x_1 of the one magnitude, there corresponds a value y_1 of the other. On a horizontal straight line (Fig. 16), starting from a point which has been chosen once for all as the zero, one then measures off, towards the right, a distance corresponding to the value of x_1, *i.e.* a distance which contains as many of the suitably chosen units of length as the amount of the numerical value of x_1. From the point x_1 the value of y_1, also in suitable units, is measured in a perpendicular direction. The point y_1 so obtained is then a representation of the quantitative relations of the two values. This process is repeated for a second pair of corresponding values x_2y_2, and a second point is thus obtained. By continuing the process, a number of such points is obtained, and if an unbroken line be now drawn through all these, a clear picture of the relation between the two variable magnitudes of the phenomenon under investigation is obtained. The horizontal lengths are called the *abscissae*, and the vertical ones the *ordinates* of the points inserted; both together are designated as the *co-ordinates*.

The method of representation employed permits also of the representation of negative magnitudes, if the rule be laid down that these shall be reckoned towards the left and downwards from zero, while the positive magnitudes are reckoned towards the right and upwards.

* **The Law of Expansion.**—In illustration, let us apply the method in the first place, to known laws of nature; the curves thereby obtained will be a representation of these functions. As a first example we may take the law for the expansion of gases by heat, the

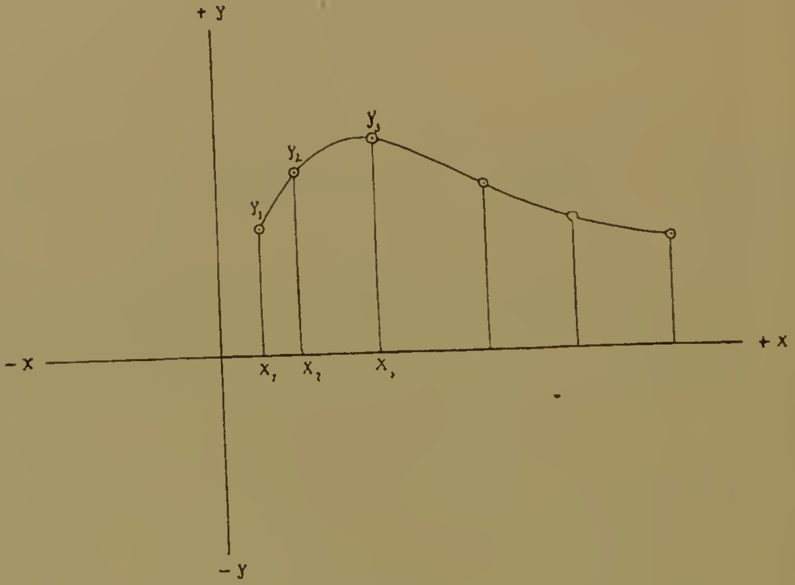

Fig. 16.

temperatures being regarded as the abscissae, the volumes as the ordinates. First of all one calculates the volumes v, corresponding to different values of t, according to the formula for constant pressure

$$v = v_0(1 + 0{\cdot}00367t),$$

assuming any definite value for the constant v_0, *e.g.* $v_0 = 1$. One obtains a table such as the following:—

t	v
0°	1·000
10°	1·037
20°	1·073
50°	1·184
100°	1·367

If we take the values of t as abscissae, those of v as ordinates, the following figure is produced (Fig. 17).

The points all lie in a straight line, and if they are joined by a straight line, one obtains from it the volumes corresponding to all the intermediate values of the temperature, and *vice versa*. Such a representation, therefore, can be used in place of the formula for obtaining the intermediate values (interpolation).

All expressions in which the two variables occur only to the first power and not multiplied with one another, represent straight lines. They are called functions of the first degree, or, in consideration of the representation just found, *linear* functions. Such functions have the general form $y = ax + b$, where a and b are constants; b representing the value which y assumes when $x = 0$. (In the foregoing example b represents the volume of the gas at the temperature 0° C.) The meaning of a is obtained as follows. Applying the formula to two

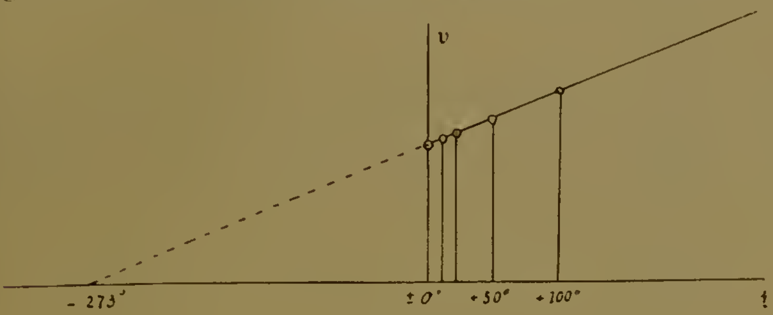

FIG. 17.

given points x_1y_1 and x_2y_2, there follows, by subtraction of the two equations $y_1 = ax_1 + b$ and $y_2 = ax_2 + b$, and rearranging—

$$a = \frac{y_2 - y_1}{x_2 - x_1}.$$

Here, $y_2 - y_1$ and $x_2 - x_1$ are the changes which y and x have simultaneously experienced; a denotes, therefore, the ratio in which the two magnitudes vary with one another. The readily intelligible meaning of the factor a in the above example is that of the *coefficient of expansion*, 0·00367, the ratio between the increase of the unit of volume and of the temperature.

If the straight line which expresses the relation between temperature and volume be produced, it cuts the horizontal axis at the point $t = -273$. At this point the ordinate v has the value zero; at this temperature, therefore, the gas would occupy the volume 0, *if it obeyed the law as far as that point.* This representation gives, as can be seen, a clear idea of the absolute zero. Since no gas has been investigated to such a low temperature as this, the prolongation of the line is not the expression of observed facts, but either has a formal meaning, or expresses a more or less probable *supposition*. Such a procedure is known as *extrapolation*, and one must always bear the doubtful nature of its results in mind. In the present case the supposition would be wrong, since most gases already change their physical state in the known ranges of temperature above the absolute zero, and become liquid or solid.

* **Representation of Boyle's Law.**—The relation between the volume and pressure of a gas at constant temperature is represented by the formula $pv = C$, where C is a magnitude which varies with the amount of the gas and with the temperature, but for given values of these remains constant. The expression is, evidently, not one of the first degree with respect to p and v, since it contains a product of the two, but is of the second degree. Accordingly, it will not be represented by a straight line. Assuming the constant $C = 100$, one obtains the following table:—

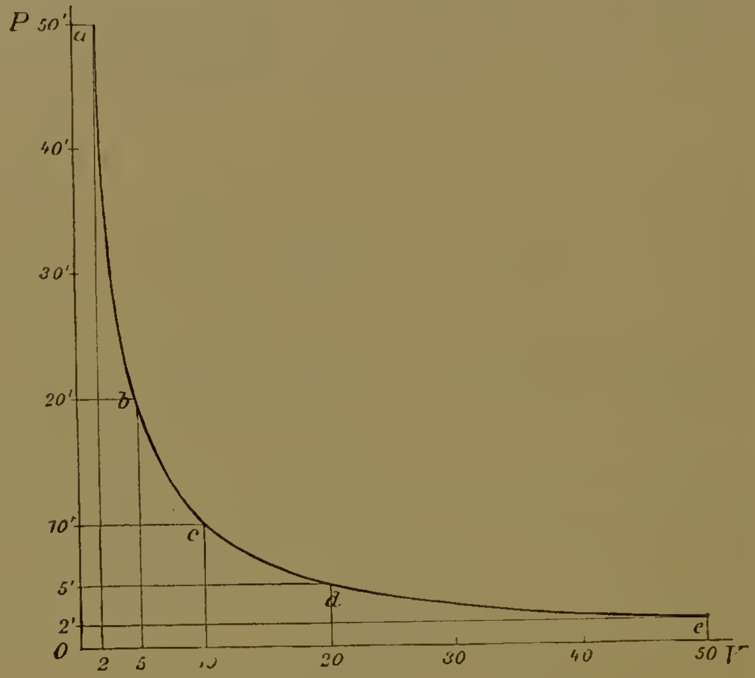

FIG. 18.

p	v
1	100
5	20
10	10
20	5
100	1

The geometrical representation gives the curved line of Fig. 18, which is called a rectangular hyperbola. The two branches approach the axes more and more, without ever touching or cutting them. Straight lines which possess this property with relation to a curve, are called *asymptotes;* and the manner of approach is called *asymptotic.* Since, simultaneously with the approach to the one axis, the curve becomes more and more distant from the other, this relation is an expression of the fact that the volume of the gas never becomes zero, however great the pressure, and, likewise, the pressure never becomes zero, however great the volume. However, the extension of this conclusion indefinitely, would again be an extrapolation (p. 75), to which the corresponding dubiety would attach.

Density of Oxygen.—After these long but necessary preliminaries, we can calculate, from the observed volume v of the oxygen at the temperature t and under the pressure p, its "reduced volume" v_o at 0° and under the pressure p_o (equal to the pressure of one atmosphere or 76 cm. mercury), by means of the formula

$$v_o = \frac{pv}{p_o(1 + at)} = \frac{pv}{76(1 + 0 \cdot 00367t)}.$$

According to the very exact measurements of Morley, the weight of 1 cc. of oxygen under normal conditions, amounts to 0·0014290 gm.; its density is, therefore, 0·0014290. Conversely, 1 gm. of oxygen occupies, under normal conditions, 699·8 cc.; its extensity is, therefore, 699·8. At any other pressure p and temperature t, these values are—

$$\text{Density: } 0 \cdot 0014290 \frac{p}{76(1 + 0 \cdot 00367t)}.$$

$$\text{Extensity: } 699 \cdot 8 \frac{76(1 + 0 \cdot 00367t)}{p}.$$

Liquid Oxygen.—For a long time oxygen was known only in the gaseous state; it was only in 1877 that Pictet and Cailletet, simultaneously and independently, converted it into a liquid. This has a bluish colour and boils, under atmospheric pressure, at − 180° C. On increasing the pressure, the boiling point rises. In this way, by increasing the pressure to 50 atmospheres, the boiling point can be raised to − 118°. At a higher pressure, the phenomenon of boiling cannot be brought about at all; on the other hand, above − 118° oxygen cannot be liquefied by any pressure, however great. These extreme values at which gas and liquid can exist side by side, are called the *critical* values; 50 atmospheres is, therefore, the critical pressure, and − 118° C. or 155° A. the critical temperature, of oxygen. More exact information regarding the behaviour of substances in the neighbourhood of the critical point will be given later (Chap. XVI.).

Whereas formerly, liquid oxygen could be obtained only in small quantity after laborious preparation, C. Linde perfected a method in 1896, by means of which oxygen could be converted into the liquid state by a continuous process. The method depends on the fact that strongly compressed air undergoes cooling on expansion. The cold thus produced is then employed to cool down a further quantity of compressed air, so that when this expands a considerably lower temperature is produced; by repeating this cycle uninterruptedly, the temperature can soon be lowered so far that the expanded air becomes liquid.

From the mixture of oxygen and nitrogen thus obtained, nitrogen evaporates off first since its boiling point lies at − 194°, much lower, therefore, than that of oxygen; a mixture is left behind which becomes increasingly rich in oxygen and, at last, is almost pure liquid oxygen.

The production of liquid oxygen has, on this account, become so cheap that attempts have been made to employ it, mixed with charcoal, as an explosive.

Commercial Oxygen.—Although oxygen, in unlimited amount, is at the disposal of every one, the manufacture of oxygen for sale has, however, already become a considerable industry. This depends on the fact that the oxygen in the air is diluted with nitrogen and, therefore, in the case of combustion does not produce such a high temperature as the pure gas. Where, therefore, it is of importance to obtain very high temperatures, pure oxygen must be employed, and this must be specially prepared.

The chemical methods employed for this purpose cannot be described here. The preparation from potassium chlorate is too expensive for the manufacture on a large scale; other substances are used which, at certain temperatures, absorb oxygen from the air and, at other temperatures, give it up again.

Only the principle of one method can be described here. It depends on the easy preparation of liquid oxygen from the air (see above). From the mixture of oxygen and nitrogen produced by this method, the nitrogen is removed by partial evaporation. By using the cold hereby produced for the liquefaction of fresh portions of air, it is possible to separate the oxygen and nitrogen of the air fairly well from one another, and this, too, at a price which makes the commercial production appear remunerative.

The oxygen prepared for sale is pumped into steel cylinders under a pressure of 100 atmospheres, and can be withdrawn from them with any desired velocity by turning a screw-valve. For the purpose of continuously maintaining definite velocities in spite of the gradual emptying of the cylinder, there are pressure-reducing valves, the opening of which enlarges more and more as the pressure in the interior becomes less, and which, in this way, effect a discharge which is almost independent of the pressure. As a rule, commercial oxygen still contains 5 to 10 per cent of nitrogen.

Other Properties.—As is to be expected from the great importance of this element, the measurement of many other properties has been carried out on oxygen. Their importance is, however, as a rule, not so great that they should be separately discussed here. One of them, however, viz., the *solubility in water*, will be given, since it often comes under discussion. It is small; 1 volume of water dissolves, at 0°, 0·049, and at 20°, 0·031 volumes of oxygen. From atmospheric air, in which oxygen is present only to the extent of one-fifth, only a fifth part will be dissolved. From this it follows that at 0°, 32 gm. of oxygen require 457 lit. of water for solution, when the solution is saturated with pure oxygen. If it is saturated with air, 32 gm. oxygen would only be contained in something like 2·3 cubic metres of water.

Further, it is deserving of mention that oxygen is *paramagnetic*, *i.e.* it is attracted by a magnet, similarly to iron. On account of the small density, this property is not visible in the case of the gas; in the case of liquid oxygen, however, it can be readily observed.

Ozone.—When oxygen is exposed to the influence of electrical oscillations, its volume changes; the volume contracts and the oxygen, at the same time, assumes new properties. The experiment is best carried out in an apparatus consisting of two tubes placed one within the other, and fused together. These tubes are coated, within and without, with an electrical conductor; each coating is connected with a pole of an induction machine, and oxygen is passed in a slow current through the space between the two tubes.[1]

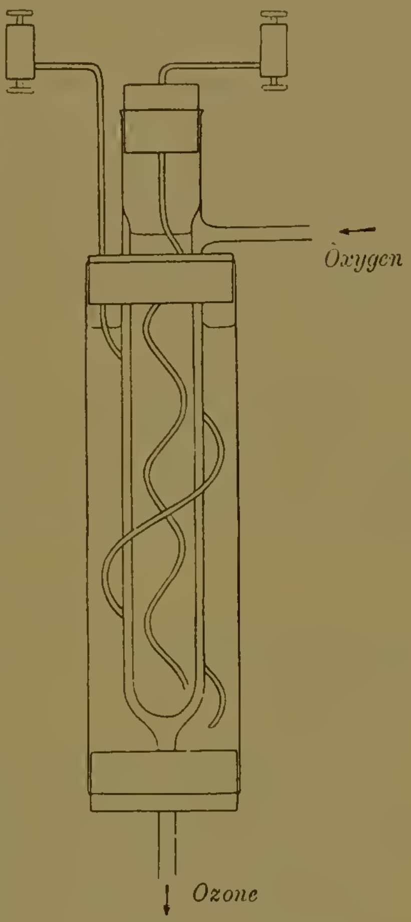

FIG. 19.

Characteristics. — That something new has been formed is evidenced first of all, by the fact that the issuing gas has a strong smell, which is irritating to the mucous membrane and induces coughing. Further, a piece of bright silver, which undergoes no change, either in air or in pure oxygen, becomes black when held in the stream of gas. Lastly, a colourless solution of potassium iodide (p. 47) becomes coloured dark brown when the altered oxygen is conducted through it, whereas ordinary oxygen has no effect. All these properties are again lost when the altered oxygen is passed through a heated glass tube.

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[1] An advantageous modification of the apparatus consists in forming both coatings of dilute sulphuric acid (which is a fairly good conductor of electricity), (Fig. 19). By means of the liquid, the apparatus, while being used, is kept cool, a condition which has great influence on the yield, since ozone is destroyed by warming, *i.e.* it is converted again into ordinary oxygen.

We here stand face to face with the fact that a simple, or undecomposable, substance assumes other properties without passing into a chemical compound by interaction with another substance. For, the glass of the electrical apparatus, with which the oxygen is in contact during its alteration, remains entirely unchanged, as also does the heated tube in which the altered oxygen again passes into ordinary oxygen.

This oxygen, endowed by means of the electrical treatment with other properties, is produced also under many other conditions. Even in very small quantity, it is recognisable by its remarkable smell, on account of which it has received the name of *ozone*.

Pure Ozone.—The oxygen in our apparatus is converted, after all, only in small part into ozone, so that the issuing gas is a mixture of oxygen with a small percentage of ozone. Pure ozone can be obtained by passing the mixture through a tube cooled by liquid oxygen; the ozone condenses then, to a liquid of a corn-flower blue colour, which passes at − 110° into a blue gas. Working with this gas is dangerous, since it readily explodes, passing, with development of heat, into ordinary oxygen.

Relation of Ozone to Oxygen.—This last fact gives us the key to the understanding of the phenomena. The heat which the ozone develops on passing into ordinary oxygen, was contained in the ozone, not, it is true, as heat, but as energy of another form, which is called *chemical energy*. We can, therefore, write the equation

$$\text{oxygen} + \text{energy} = \text{ozone}.[1]$$

By subjecting oxygen to the influence of electrical oscillations, there is transferred to it the energy which it requires for its transformation into ozone.

As is evident, ozone can be formed from oxygen only under such conditions that the necessary energy can be transferred to the latter. As a matter of fact, this is the case in all circumstances (to be specified later) which lead to the formation of ozone (*vide* Chap. XV.).

Allotropy.—Elements which, by reason of different energy-content, have different properties, are called *allotropic*. Oxygen and ozone are, therefore, allotropic modifications of the same element. The fact of the existence of allotropy follows, on the one hand, from the fact that the different forms are convertible into one another without residue, and, on the other hand, from the fact that equal weights of both forms give identical products with equal weights of other substances. Thus in the combination of a combustible substance with oxygen or ozone exactly the same compounds are obtained, and in these nothing remains of the difference between the two kinds of oxygen.

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[1] The equation is not to be thought of as expressing that ordinary oxygen contains no energy, but only that ozone contains more energy than ordinary oxygen.

Besides the difference in chemical behaviour and in energy-content, there also exist between oxygen and ozone differences in their physical properties. More especially has there to be mentioned that the density of ozone is to that of oxygen as 3 : 2. One cc. of ozone weighs, under normal conditions, 0·002144 gm., and 1 gm. of ozone occupies the volume 466·5 cc.

Technical Application.—Since ozone acts more quickly and more energetically on oxidisable substances than oxygen, it is prepared at the present day, on a large scale, by an electrical method, and is employed in the arts for bleaching, purification of starch, resinification of oils, etc.

CHAPTER VI

HYDROGEN

Preparation from Water.—Water is one of the most important and widely distributed compounds of oxygen. Besides oxygen, this substance contains another element which is called hydrogen, and which can be obtained from water by the withdrawal of oxygen. This can be done, for example, by means of red-hot iron. We have convinced ourselves (p. 64) that, at a moderately high temperature, iron combines with oxygen. If iron, in the form of thin wire, or turnings, or otherwise finely divided, be heated in a tube to redness and steam be passed over it (Fig. 20), the latter is converted into gas which can, like oxygen, be collected over water.

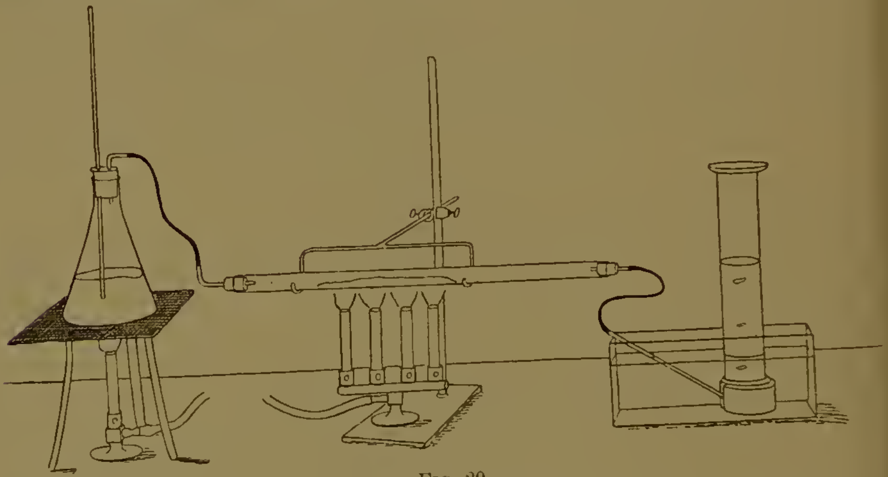

Fig. 20.

Identification of Hydrogen.—The gas which is collecte resembles oxygen in its outward appearance; like it, it is colourless odourless,[1] and tasteless, and is not dissolved by water to an appreciabl extent. It can, however, be readily distinguished from oxygen by the well-known reaction of that gas. A glowing splinter of wood does not inflame, but is extinguished. If, however, a splinter burning with a flame be brought into the gas, it also, it is true, is extinguished, but the gas itself takes fire and burns with a pale flame. Hydrogen, therefore, cannot support the combustion of wood, but is itself combustible in air.

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[1] The gas obtained from steam and ordinary iron exhibits an unpleasant smel reminiscent of petroleum. This, however, is due to the formation of other substanc from the carbon contained in ordinary iron, and does not occur when pure iron is used.

Detection of Oxygen from Water.—If the iron be afterwards examined, it will be found to be coated with a black-grey, friable mass which has the same properties as the substance produced by the burning of iron in oxygen, and is, in fact, like it, an oxide of iron. The following process, therefore, occurs:—

water + iron = hydrogen + oxide of iron.

Other Methods of Preparation of Hydrogen.—The experiment just described is of great historical importance since it served, in its day, to prove the compound nature of water (which was formerly regarded as an element). It yields, however, little hydrogen and is inconvenient to carry out.

The experiment becomes much easier when, instead of iron, a metal is used which decomposes the water even at a low temperature. This decomposition occurs with the light metals, *e.g.* magnesium. If water be poured over magnesium powder, such as is, at present, much sed for the production of a bright, sudden light in photographing, no ction, certainly, takes place at the ordinary temperature; on heating, owever, till the water boils, a gas is slowly evolved which can be ollected in the ordinary way, and can be shown to be hydrogen by its urning with a pale-blue flame.

The evolution of gas can be greatly accelerated by dissolving in he water a little magnesium chloride, a salt-like compound of nagnesium. This does not take any part in the reaction but only issolves the oxide of magnesium which is formed, and thus frees the urface of the metallic particles from the coating of this substance, y which the action of the water is retarded.

Lastly, there are light metals which decompose water with energy, ven at the ordinary temperature. This is the case, for example, with odium (p. 52). On bringing a little of this metal in contact with ater, an energetic action takes place whereby so much heat is eveloped that the metal melts. For the purpose of collecting the s hereby produced, one can proceed as follows.

A little sodium is placed on the water in the trough and pressed nder the surface with an inverted spoon made of fine wire-gauze ig. 21). The evolved gas then ascends through the meshes of the uze, while the metal is kept back. If the spoon be placed under an verted tube, filled with water and standing in the trough, the gas n be collected and be shown to be hydrogen.

Also, the sodium may be wrapped in blotting-paper, and quickly brought under the mouth of the tube by means of a tongs. The water then penetrates only after some moments to the sodium, and this rises within the tube, where it acts on the water and evolves gas. In this case, also, the gas can be shown, by its combustibility, to be hydrogen.

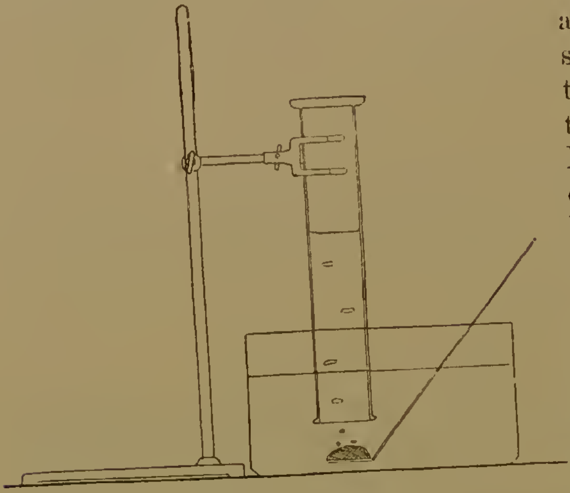

FIG. 21.

As a rule, the gas so obtained burns not with a blue but with a yellow flame. This is due to the presence of drops of liquid, which contain the sodium compound which has been formed; to this the flame owes its yellow colour. If one wishes to avoid this, the gas must be allowed to stand some time till the drops of liquid have settled and the gas has become free from fumes.

Chemical "Forces."—If the methods by which oxygen was obtained are compared with those employed for the preparation of hydrogen, an essential difference is found. Oxide of mercury and potassium chlorate decompose at moderately high temperatures into oxygen and the other constituent, without the participation of any other substance. Hydrogen, however, was obtained, not by the other constituent of water being separated as an element, but by its entering into another compound, and the formation of hydrogen from water takes place all the easier the more energetically the combination of the oxygen with the substance added takes place, *i.e.* the more stable the newly formed compound is.

Similar conditions are also met with in many other cases. If we have a compound of the substances A + B, and bring into contact with it the substance C which can combine with A to form a very stable compound, then this compound A + C is formed along with the substance B.

For a long time the following picture was made of these relations—a picture which is still much used, although there are importan points where it does not prove to be correct. The various substance were imagined as being endowed with forces, in virtue of whic they could mutually bind one another. If, now, the force betwee A and C is greater than that between A and B, C must decompos the compound A + B, when both come together; A is bound held fast by C, and B is displaced from its compound with A and free.

In the case under discussion, it was assumed that the force between hydrogen and oxygen is smaller than that between iron and oxygen; if, therefore, water is exposed to the action of iron, the smaller force is overcome by the greater, and the stronger iron drives out the hydrogen from the water.

A more exact knowledge of chemical processes has shown that this picture is not a suitable one; it represents, only quite roughly, some of the actual relations, but is contradictory to other facts. Through long use in chemistry, however, this mode of expression has become to such an extent a part of the daily language of that science, that a knowledge of it is necessary for the understanding of chemistry, although it is better not to use it. A more suitable exposition of such processes will be given shortly (p. 99).

Preparation of Hydrogen from Acids.—None of the experiments we have described for obtaining hydrogen from water are convenient to carry out, especially when comparatively large quantities of the gas have to be prepared. For this purpose, not water but other compounds of hydrogen are decomposed.

Among the compounds of hydrogen there is an especially large and important group known as the *acids*. These are hydrogen compounds which have the property that their hydrogen is liberated when they are acted on by certain metals. The strength of the action varies with the nature of the acid and of the metal, and as there is a great variety of acids and metals, the ones most suitable for the purpose on hand can be chosen.

Zinc (p. 55) is the most suitable metal and hydrochloric acid the most uitable acid. When these are brought ogether, a vigorous reaction takes place even at ordinary temperatures, and by his means hydrogen in any desired mount can be generated.

The apparatus employed for this purpose can be arranged in very different ways. In Fig. 22 a very useful form is hown. The zinc is contained in a bottle, t the bottom of which it is convenient o have a second tubulure closed by a ork and stop-cock. Into the neck of the ottle there is inserted, air-tight, a oubly bored cork, through which pass a ropping-funnel and a short glass tube. dropping-funnel differs from an ordinary funnel in that it is urnished with a tap by means of which the liquid it contains an be allowed to flow out as desired, or be kept back. To the gas-

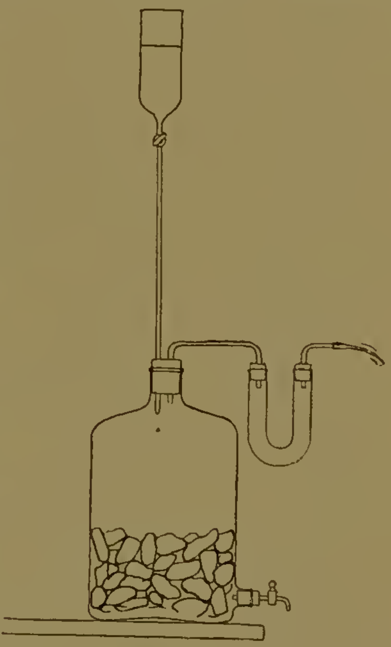
FIG. 22.

delivery tube there is attached an indiarubber tube, to which the rest of the apparatus is connected.

When it is desired to generate hydrogen it is only necessary to fill the dropping funnel with hydrochloric acid, and to carefully open the tap, so that the acid reaches the zinc in single drops. Each drop forthwith evolves gas, and by regulating the tap any desired velocity of evolution may be obtained. When no more gas is required the tap is completely closed and the apparatus is ready for use when next required. When the bottle is nearly filled with liquid, this is run off by the tap at the bottom.

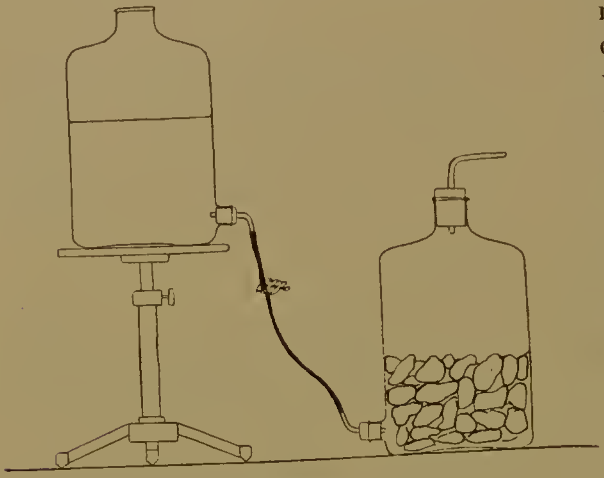

FIG. 23.

In some cases it is expedient to replace the dropping-funnel by a second bottle with a tubulure at the bottom. This is connected, so as to allow of easy movement, with the bottom tubulure of the first bottle by means of indiarubber tubing. On the indiarubber tubing there is placed a clamp of brass wire, a "pinch-cock," which presses the tubing together and closes it. The second bottle is filled with hydrochloric acid and placed above the first (Fig. 23). By means of a screw, the pinch-cock is opened wide enough to allow the acid to flow to the zinc in drops, whereupon the evolution of hydrogen begins and can be regulated as desired.

Another form which, although not so suitable, is still much used, is shown in Fig. 24. The Kipp apparatus, so called from the name of its inventor, consists of the under vessel AB, which is double, and either part of which has a lateral tubulure, and of an upper globe-shaped funnel C, the long stem of which reaches down to the under part of A and is ground into the neck of B. The zinc is placed in B, the acid in C; the gas-delivery tube is fixed in the lateral opening of B and closed by a tap. The method of working is as follows.

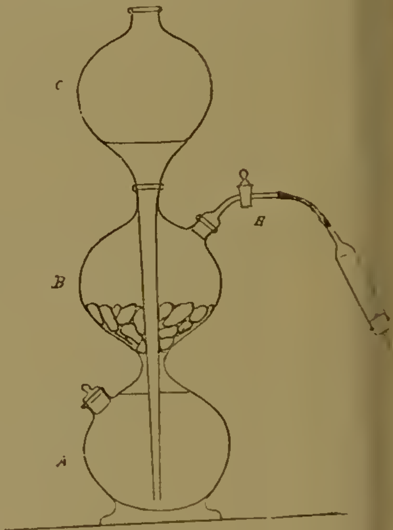

FIG. 24.

On opening the tap H the air in the apparatus first of all escapes; the acid flows from C into A and, when A is filled, comes into contact with the zinc in B. Evolution of gas begins forthwith, and the hydrogen which is generated escapes through the tap H. If more gas is developed than can pass through the tap, the acid is forced back out of B into A and C; it comes out of contact with the zinc and the evolution of gas is interrupted or diminished. On the other hand, if more gas is withdrawn the acid passes back to the zinc and the evolution of gas takes place more quickly.

Although this automatic regulation is an advantage, the apparatus has the disadvantage that the fresh acid from C is mixed with the partially spent acid in A, and its action thus interfered with. The full effect of the acid can, therefore, never be obtained, as can be done with the apparatus first described.

Drying of Gases.—The hydrogen, which can in this way be obtained in any desired quantity, is not quite pure, since it takes up water vapour from the aqueous liquids in the presence of which it is produced. To free it from this, the gas is passed over substances which retain the water. There are many such desiccating agents. One of the most convenient is calcium chloride, a white, very hygroscopic salt which is formed as a waste secondary product in many chemical manufactures, and is, therefore, very cheap. A tube is filled with this salt and placed in the path of the hydrogen, the simplest way being to attach the tube directly to the generating apparatus, as ndicated in Figs. 22 and 24.

Concentrated sulphuric acid is another and much more effective desiccating agent. Since this is a liquid it is either placed in a wash-bottle (Fig. 25), in which the gas is made to bubble through the liquid, or spread out over some material which has a large surface and is not attacked by the acid, such as broken glass or, better, pumice-stone. It can then be placed ike a solid substance in tubes, and in this case one must only bear in mind that the volume of the acid ncreases through its attracting water and flows down o the lowest parts of the apparatus. A collecting-chamber for this acid must, therefore, be provided. In Fig. 26 is shown a drying-tower which is intended or large quantities of gas, and which fulfils these requirements; it can also be used for calcium chloride.

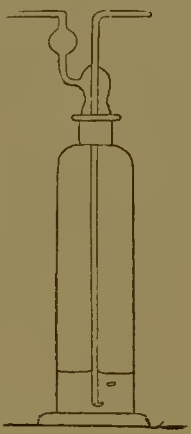

FIG. 25.

Besides the aqueous vapour, the hydrogen frequently contains also very fine drops of the liquid rom which it has been evolved (p. 84). These pass through wash-bottles, but are retained, with certainty, by a plug of cotton wool.

Other impurities which are usually contained in the hydrogen will not occupy us here, since they are mostly of no account for the experiments which are to be performed. By these traces of foreign substances, only the fact that pure hydrogen is completely odourless, is masked; impure hydrogen has a slight odour, which it loses, however, by appropriate purification.[1]

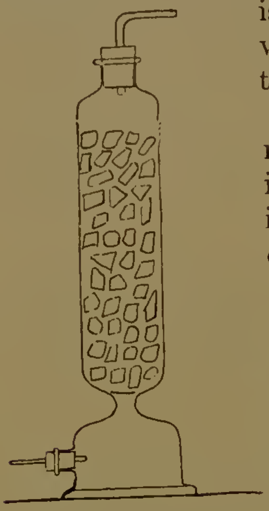

FIG. 26.

Physical Properties of Hydrogen.—The most conspicuous property of this element is its small density; of all known substances it has, as has already been said, the smallest density.

If a flask of about a litre capacity, closed by a stopper and good-fitting glass tap, be weighed, first filled with air and then evacuated, a difference of weight of rather more than 1 gm. is found. If the exhausted flask be filled with hydrogen under atmospheric pressure, the increase of weight amounts to only about 0·1 gm.—if anything, rather less. This shows that hydrogen is at least ten times as light as air. By exact experiment the ratio is found to be 1 : 14·4.

On comparing the weights of like volumes of oxygen and hydrogen at 0° and under a pressure of 76 cm., the ratio is found 15·88 : 1 or 16 : 1·008.

Since 1 cc. of oxygen under normal conditions weighs 0·001429 gm., the weight of 1 cc. of hydrogen, or its absolute density under normal conditions, must be 0·0000900.

Molar Weight.—This ratio holds, in the first place, for the two gases under normal conditions. On account, however, of the identity of the laws of pressure and temperature in the case of all gases (pp. 68 and 69), it remains unchanged when the densities of oxygen and hydrogen are compared at any pressure and temperature, supposing only that both gases are at the same temperature and pressure. When, therefore, the weight of a gas at any pressure and temperature is compared with that of the same volume of a *normal gas* under the same conditions, a constant ratio-number is obtained which is independent of the pressure and the temperature, and is determined only by the nature of the gas.

For such a normal gas there is taken, not an actual substance but an imaginary gas which is 32 times as light as oxygen. The historica development which has led to the choice of this particular number will be given later (Chap. VII.). For the present, it is sufficient to state the fact.

The ratio of the weight of a given gas to that of an equal volume of the normal gas under the same conditions, is called its *molecula*

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[1] The purification can be effected by means of potassium permanganate contained i a wash-bottle through which the gas passes.

weight or its *molar weight.* Since the former name has been derived from certain hypothetical notions regarding the constitution of the gases, notions which are not essential to the actual facts, we shall give preference to the name molar weight although, at present, the other is still the one most used.

Since the normal gas is taken as 32 times lighter than oxygen, its absolute density under normal conditions, *i.e.* at a pressure of 76 cm. and 0°, is equal to 0·00004466 gm. and its extensity to 22400 cc. Both numbers are of great importance and find manifold application.

The molar weight of a gas is got, therefore, by dividing its weight G by the weight of an equal volume v of the normal gas under the same pressure p and at the same temperature t. This weight g is found, according to the formula on p. 72, to be

$$g = 0{\cdot}00004466\frac{pv}{76(1 + 0{\cdot}00367t)}.$$

The volume is here measured in cc. and the pressure in cm. mercury. If G is the weight of the gas, the molar weight is, according to definition, G/g, or, introducing the value of g, the absolute temperature $T = 273 + t$, and collecting all numerical factors,

$$\text{molar weight} = 6232\,\frac{TG}{pv}.$$

According to definition the molar weight of oxygen is 32. From the data given above for hydrogen, it follows that the molar weight of hydrogen is 2·016.

The molar weight of a gas can also, according to this, be regarded as the weight of that amount of gas which occupies the same volume v, under the same pressure p and at the same temperature t, as 1 gm. of the normal gas. From the equation $pv = rT$ or $pv/T = r$, we see that the constant r depends only on the pressure, volume, and temperature; it assumes, therefore, the same value for different gases, when these magnitudes are equal. From the definition of molar weight just given, it therefore follows that *the constant* r *must have the same value for a molar weight of any and every gas*, independent of its nature. The constant referred to the molar weight is called R.

To calculate the value of this, we apply the equation $pv/T = R$ to the normal gas at 0° and under atmospheric pressure. In this case, $v = 22400$ cc., $p = 1013130$ in absolute units (p. 67), and $T = 273$. Hence $R = 8{\cdot}31 \times 10^7$ in absolute units.[1] The equation

$$pv = RT = 8{\cdot}31 \times 10^7T$$

holds good, therefore, for a molar weight of any and every gas.

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[1] If the pressure is reckoned in atmospheres, $p = 1$ and $R = 82{\cdot}1$. If p is reckoned in gm. on 1 sq. cm. $p = 1033$ (p. 67) and $R = 8{\cdot}48 \times 10^4$. It is best to keep to absolute measure.

* It must, however, be noted that the general gas law, as well as its part-laws (that of Boyle and of Gay-Lussac), *is not entirely exact.* On the contrary, all gases deviate more or less from it, the deviation being all the smaller the more dilute the gases are. We are dealing here, therefore, with a "*limiting law*" (p. 20), to which the actual substances approximate, but which they never entirely fulfil.

* Under ordinary conditions of temperature and pressure, these deviations are, in the case of most gases, small and amount to scarcely one-hundredth of the theoretical value. A gas which would completely obey the law $pv = RT$, is called an "ideal gas." The normal gas above mentioned is assumed to be an ideal gas.

* Since, formerly, the densities of gases were, almost exclusively, referred to the density of air as the unit, it is necessary to establish the ratio of our molar weight to these numbers. Now, a litre of air weighs 1·293 gm.; it is, therefore, 28·9 times as heavy as the normal gas. To calculate the molar weight from a density referred to air, the latter must be multiplied by 28·9; in the reverse case, the number must be divided by 28·9.

Experiments.—The small density of hydrogen can be demonstrated in various ways. A small balloon of collodium, goldbeater's skin, or caoutchouc, is filled with hydrogen and allowed to go free. Since hydrogen is, in round numbers, fourteen times as light as the displaced air, it experiences a corresponding upward force amounting to about 1 gm. for every litre, and the balloon, therefore, quickly ascends. The same thing can be shown by blowing soap-bubbles with hydrogen and allowing them to ascend.

This property is made use of on the large scale for making aërial balloons, which are, essentially, bags of silk rendered air-tight and filled with hydrogen. The total load which such a balloon can carry (inclusive of its own weight) is found, according to what has been stated, to be, in round numbers, 1 kilogm. for each cubic metre. This holds, however, only in the neighbourhood of the earth's surface; the higher one ascends, the less dense does the air become and the less its buoyancy.

This property of hydrogen can be demonstrated in another way. Two glass cylinders are filled with the gas over water and supported in an upright position—one with the mouth upwards, the other with the mouth downwards (Fig. 27). If, after a few moments, a flame be brought near both cylinders, the inverted one will be found to be still filled with hydrogen while the other contains only air.

Behaviour of Hydrogen at Higher Pressures.—In its properties as a gas, hydrogen, of all known substances, approximates most nearly to the "ideal" gaseous state. On closer investigation, however, a deviation is found, such that with increasing pressure, the volume of hydrogen diminishes *less* than it ought to according to Boyle's law. This deviation increases as the pressure becomes greater, following a very simple law which can be expressed as follows.

The total volume of hydrogen is made up of one part which strictly follows Boyle's law, and of another part which is independent of the pressure. Denoting the total volume by V, and that part which obeys Boyle's law and for which, therefore, at constant temperature, the equation $pv = C$ holds good, by v, and denoting by b the other part which is independent of the pressure, we have $V = v + b$. Substituting for v in the equation $pv = C$ its value $V - b$, we obtain $p(V - b) = C$ as the expression for the behaviour of hydrogen at all, and especially at high, pressures.

A clear picture of the substance of this law can be got by imagining the hydrogen to consist of small particles of greater density, between which is an empty space. The latter would obey Boyle's law, while the former would represent the incompressible part of hydrogen.

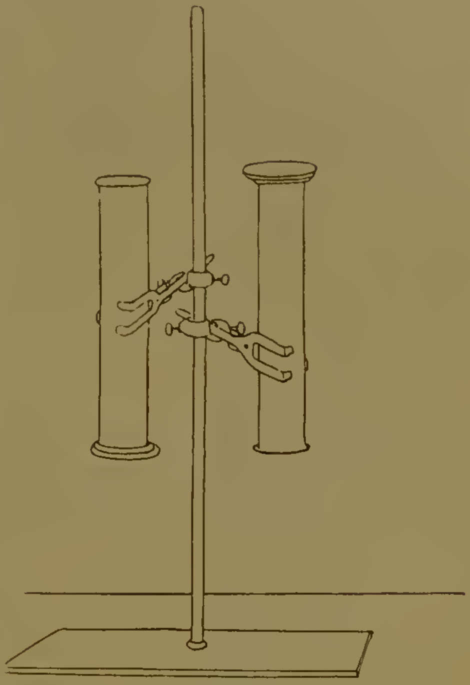
Fig. 27.

In the case of hydrogen at 0° and under atmospheric pressure, the value of b amounts to 0·00062 of the total volume.

The equation $p(V - b) = C$ shows that the diminution in volume is smaller the more the pressure increases, and that when the pressure is very high, V can be only slightly greater than b. In this case, hydrogen behaves almost like a liquid, for a liquid also has the property that its volume only slightly diminishes with great increase of pressure.

* In the case of the other gases, the deviations from the law $v = RT$ are generally such that the gases are, at first, *more* compressible than according to Boyle's law. At very high pressures, however, they all behave similarly to hydrogen.

Liquid Hydrogen.—By the application of very effective cooling arrangements, the principle of which has been pointed out on p. 77, it has recently become possible to observe hydrogen in the liquid state. It appears as a colourless liquid, the density of which at its boiling point is only 0·07, but which, nevertheless, forms a quite visible surface and exhibits, in all respects, the behaviour of a liquid substance. Hydrogen boils under atmospheric pressure at −252·5°, or only 20·5 above the absolute zero; by allowing it to boil under reduced pressure, this temperature can only be slightly lowered. At this temperature, all liquids and gases[1] (oxygen and air as well) are transformed into solid bodies, the vapour pressure of which is exceedingly small. Thus, for example, if the closed end of a bent tube, filled with air, be placed in a vessel of liquid hydrogen (Fig. 28), the upper part at once becomes free from air and shows a vacuum such as can scarcely be obtained with the very best pumps.

Diffusion.—If two cylinders with even-ground, broad rims are placed air-tight on one another with the help of a little grease (Fig. 29), after the upper one has been filled with hydrogen, one would expect that the lighter hydrogen would remain above and leave the heavier air underneath. If, however, on the following day, the two cylinders be carefully separated from one another and immediately closed by glass plates which are held in readiness, hydrogen will be found in both. For if a flame be brought near, the gas contained in both cylinders takes fire, and the pale hydrogen flame rushes with a whistling noise along both cylinders.[2]

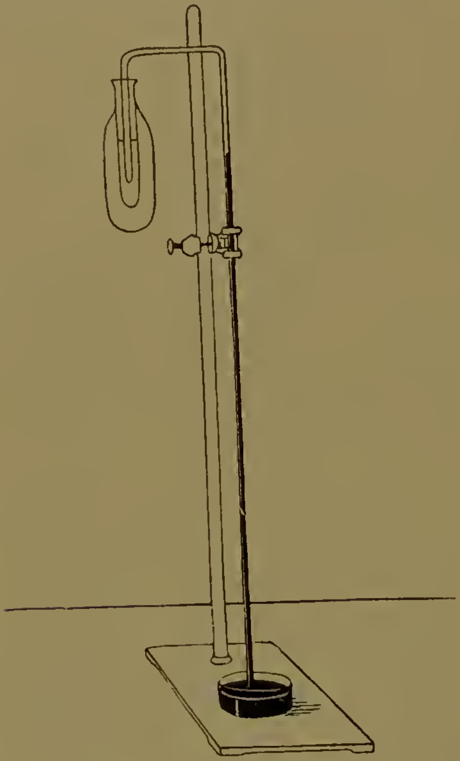
FIG. 28.

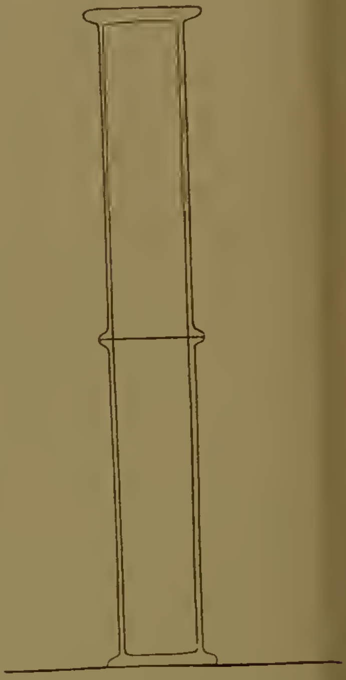
FIG. 29.

This mutual spreading of the gases into one another is called *diffusion*. It is a quite universal phenomenon; all gases diffuse into one another and the diffusion goes on until each gas is uniformly distributed throughout the whole space.

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[1] With the exception of helium; cf. p. 45, footnote.—Tr.

[2] The fact that the combustion of hydrogen here exhibits other phenomena than usual, is due to admixture with air, and will soon be explained in detail.

Dalton's Law of Partial Pressures.—Different gases, therefore, which are present in the same space, behave as if each were there alone, for each separately obeys the law that in a given space a gas is not at rest until it fills the space uniformly. *For gaseous equilibrium, therefore, not the total pressure, but for each gas only its partial pressure, i.e. the pressure which it would exert if it alone occupied the space, is of account.*

This is a fact of great importance, since many other phenomena exhibited by gases are determined by the partial pressures of these. Thus, for example, the partial pressure is the determining factor for gaseous equilibrium in chemical processes, which will be considered later.

In order to express these relations for the purpose of calculation, one has only to take into account that the total pressure of a gaseous mixture is the sum of the partial pressures, and that each gas present is uniformly distributed throughout the space, the total volume being, therefore, equal to the volume of each gas. If, therefore, P is the total pressure and V the total volume, the values for the single gases being denoted by p_1, p_2, p_3, . . . and v_1, v_2, v_3, . . . we have the equations

$$p_1 + p_2 + p_3 + \quad . \quad . \quad . \quad = P$$

and $v_1 = v_2 = v_3 = \ldots = V$.

The law of partial pressures which has just been stated was established by Dalton and is called after him. It is a special case of a more general law, according to which, in any given gas mixture (the components of which do not chemically interact), each single gas behaves, with respect to all its properties, as if it were alone present in the total space under a pressure equal to its partial pressure. We shall have many opportunities later of becoming acquainted with individual cases of this general law.

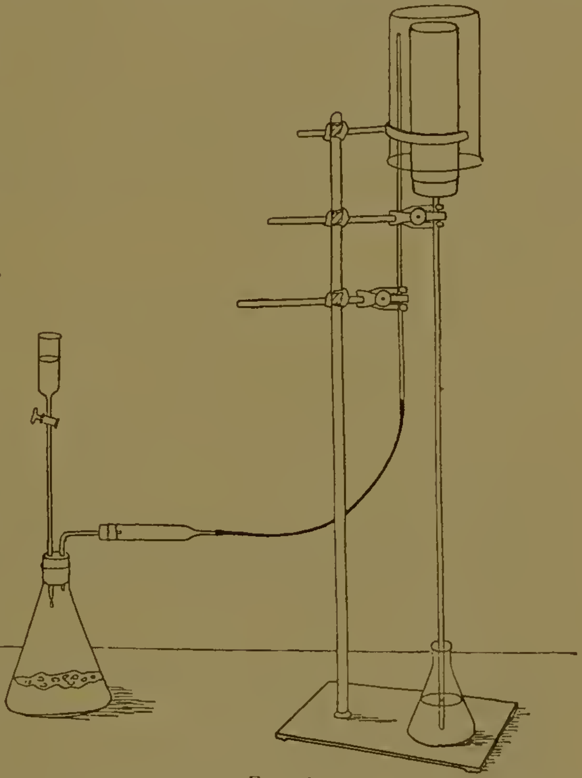

Fig. 30.

Velocity of Effusion.—A cell of porous clay, such as is used in galvanic batteries, is closed by a cork through which passes a glass tube 1 metre long (Fig. 30). This tube dips into a vessel containing (coloured) water, and a beaker is inverted over the clay cell. If, now, a rapid current of hydrogen be passed into the beaker, a stream of bubbles is seen to pass out of the lower end of the tube, which shows that the pressure in the interior of the cell has suddenly increased. In a short time this ceases and equilibrium is established.

If the beaker be now removed, the water ascends just as quickly in the tube, a sign of decrease of pressure in the cell. The water attains a certain height and then sinks again, since the porous cell cannot maintain a permanent difference of pressure.

These phenomena are due to the fact that hydrogen passes much more rapidly than the other gases, *e.g.* air, through small openings such as the pores of the clay cell. When, therefore, the cell is surrounded with hydrogen, as in the first part of the experiment, this gas penetrates rapidly into the interior, since its partial pressure there is zero. For the same reason, the air passes at the same time out of the cell into the hydrogen outside. The movement of the hydrogen takes place, however, much more quickly, and, therefore, an excess of pressure is produced in the interior of the cell, which drives the air out of the tube in bubbles. Equilibrium occurs when the gases on both sides of the cell-wall have the same composition.

If, now, the external hydrogen is removed, the same processes are repeated in the reverse sense; the hydrogen, on account of the difference of the partial pressures, passes outwards, and it does so more quickly than the air can penetrate inwards; hence the diminution of pressure.

* Differences of velocity, similar to those which are here found in the case of effusion through the pores of the clay, are seen in the case of the diffusion of two gases into one another, without a separating partition. Both kinds of movement are, indeed, similar, but we are not dealing with quite the same phenomenon in both cases. We shall only remark, generally, that hydrogen diffuses more rapidly than all other gases, and that the velocity of diffusion is, in general, all the smaller, the greater the density of the gas.

* **The Law of Effusion of Graham and Bunsen.**—The experiment on the differences of the velocity of effusion of gases in the form we have just been considering, is not suitable for quantitative determinations. The following, however, is a suitable form.

The apparatus in Fig. 31 is a gas-measuring tube set in a liquid and having two marks m_1 and m_2. At the upper end there is a tap, which, however, does not open free into the air, but into a space closed by a thin platinum plate pierced with a fine hole. If the tube is filled to somewhat below the mark m_1 with gas and the tap opened, the gas is forced through the fine opening, and the time can be noted which elapses till the liquid passes from the lower to the higher mark.

If mercury be used as the liquid, the lower mark cannot be seen in the case of the arrangement shown in Fig. 31. In this case a U-tube is used, as indicated in Fig. 32.

If the experiment is carried out with different gases under the same conditions, it is found that the times of effusion of equal volumes through the same opening are to one another as the square roots of the densities. In other words, the *velocities* of effusion are inversely proportional to the square roots of the densities.

This law and the apparatus described can, therefore, be made use of for the purpose of measuring the ratios of the densities of different gases. This method is employed in coal-gas works, because conclusions can be drawn as to the value of the gas from determinations of the density.

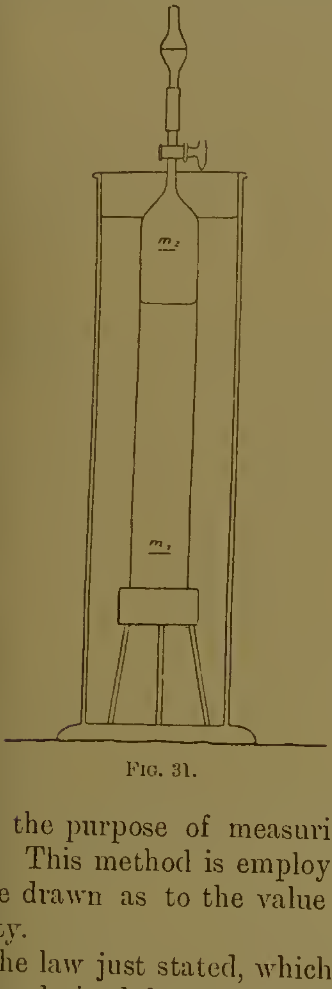

Fig. 31.

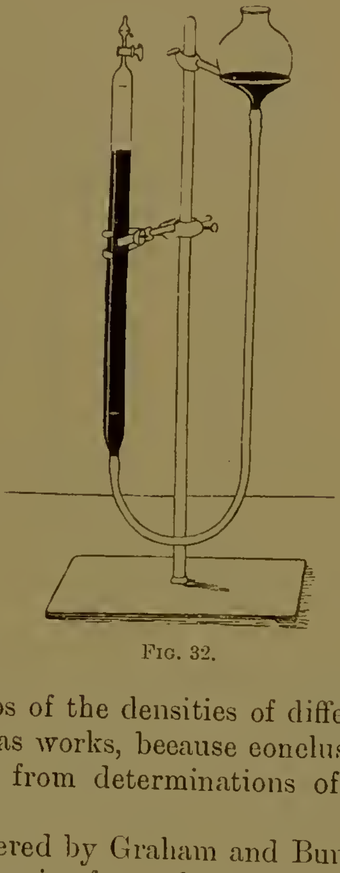

Fig. 32.

The law just stated, which was discovered by Graham and Bunsen, can be derived by the principles of dynamics from the conditions of experiment. The enclosing liquid performs in all the experiments he same amount of work, filling up, by reason of the existing excess of pressure, the space between the two marks. This work is converted nto the kinetic energy of the gas. The latter is represented by the ormula $\frac{1}{2}mc^2$, where c is the velocity and m the mass (p. 23). If we ompare two gases which we distinguish by 1 and 2, we must have $\frac{1}{2}m_1c_1^2 = \frac{1}{2}m_2c_2^2$. The densities d are proportional to the masses, equal volumes being used in the experiments; we therefore have $d_1c_1^2 = d_2c_2^2$ or

$$c_1 : c_2 = \sqrt{d_2} : \sqrt{d_1}.$$

* **The Spectrum of Hydrogen.**—When electrical discharges are allowed to pass through a glass tube containing hydrogen under a pressure of a few millimetres of mercury, the hydrogen becomes incandescent and emits light.

The experiment is usually carried out in tubes of the form shown in Fig. 33. Into the wider portions platinum wires are scaled which effect the conduction of the electric current. In the narrower portion between, where the current is condensed to a small cross-section, the hydrogen glows most strongly.

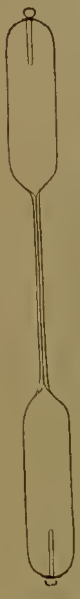

Fig. 33.

The light emitted by hydrogen, made to glow electrically, appears rose-red to the naked eye. If, however, the streak of light be viewed through a prism held with the refracting edge parallel to the streak, not one line but three separate lines, a red, a green, and a violet, are seen. The last is the most difficult one to see.

This phenomenon is due to the fact that the different kinds of light on passing through a prism are deflected to a varying extent. The appearance of three separate lines is, therefore, a proof that the hydrogen light consists of three kinds of rays—red, green, and violet. This light behaves differently from that which comes from ordinary flames and glowing bodies; for if the latter be viewed through a prism a streak of light is found to be drawn out to a broad band, the spectrum, in which are represented side by side all possible kinds of light from red to violet.

The appearance of these three lines is a property of hydrogen which is possessed by no other substance. The same lines also appear when hydrogen is made to emit light in any other way, and their appearance is not prevented by the presence of other substances so long as these do not completely convert the hydrogen into other compounds. Since this scarcely occurs at the high temperatures used, these lines, the "spectrum of hydrogen," are an excellent criterion for its presence in a glowing gas-mixture.

In this way one can recognise not only the terrestrial hydrogen, but the same lines are found in the so-called protuberances of the sun, *i.e.* torch-like formations which rise above the edge of the sun and can be observed, more especially, during eclipses of the sun. Thi is a proof that hydrogen occurs in large quantities on the surface o the sun, and that it occurs in the free state.

The hydrogen lines can, likewise, be recognised in the spectrum o many stars, so that this element, by reason of the light effect peculia to it, has been shown to be distributed throughout the whole o space.

The ordinary light of the sun and of many stars exhibits *black* lines at exactly the same points of the spectrum at which the hydrogen lines appear *bright*. Both kinds of lines are very closely related to one another. At a later stage we shall enter in detail into the relation between them; we would only mention here that these black lines prove the presence of hydrogen with the same certainty as the bright ones. It is, indeed, the same phenomenon appearing under different conditions.

Hydrogen burns to Water.—As a test for hydrogen, its combustibility in air has been used. The question as to what thereby becomes of the burning hydrogen can be answered with the knowledge

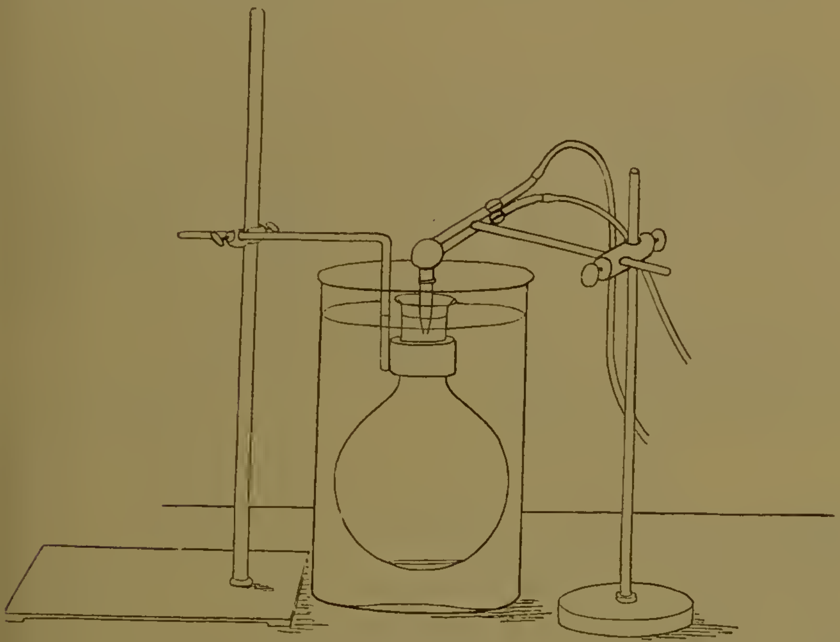

Fig. 34.

ve have already gained. We have seen that iron and sodium, by cting on water, pass into oxygen compounds, whereby hydrogen is ormed. According to this, water is a compound of hydrogen and xygen, and since combustion consists in a combining with oxygen, we hould expect water to be the product of the combustion of hydrogen. s a matter of fact, we can convince ourselves by direct experiment hat water is the product of combustion of hydrogen.

If a large, dry beaker be held over the flame of burning hydrogen, dew is quickly formed which looks exactly like the film of moisture n a cold window-pane, and behaves like it. Special arrangements re necessary if it is desired to collect the water in larger quantities.

In Fig. 34 a burner is represented (cf. p. 102) in which, by means f pure oxygen conveyed to it, hydrogen can be burned. Since large mounts of heat are hereby produced, the burner is placed in a wide glass flask which can be cooled by surrounding it with water. If this apparatus is put in action, a few cc. of a colourless liquid soon collect, which, in all its properties, shows itself to be pure water.

Combustion of Hydrogen by means of Oxygen Compounds.—For the formation of water it is not necessary that the oxygen be presented as such to the hydrogen; oxygen compounds, or oxides, can also be used for the purpose. If hydrogen be passed over oxide of mercury placed in a bulb-tube (Fig. 35), no action, certainly, takes place at ordinary temperatures; so soon, however, as the oxide of mercury is slightly heated metallic mercury makes its appearance, and water is deposited on the colder parts of the tube, first as dew, and then in small drops.

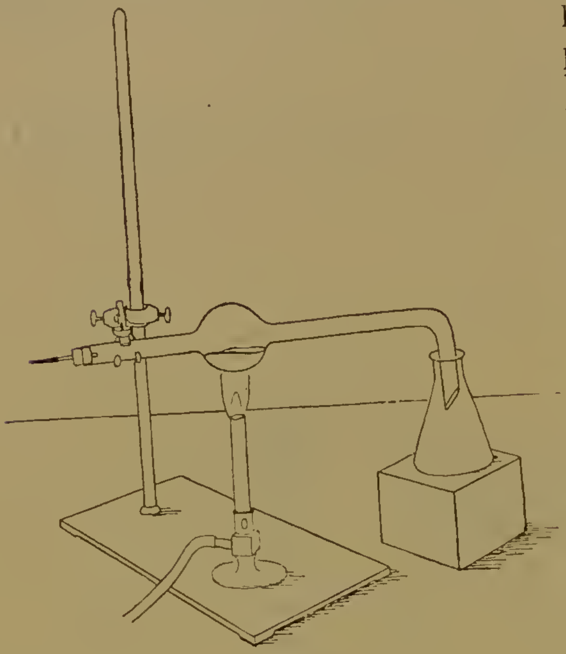

FIG. 35.

Quite similar phenomena are observed when the oxides of other metals are used in place of oxide of mercury. By heating oxide of lead in a current of hydrogen metallic lead and water are obtained. The oxide of lead, under the name of litharge, is obtained in large quantities by heating metallic lead in air, the lead hereby combining with the oxygen contained in the air. When copper oxide, obtained by strongly heating copper in air, is heated in hydrogen, red metallic copper and water are produced. Hydrogen may, therefore, be used for the purpose o obtaining the metals from their oxides. This method finds n application on a large scale, because there are cheaper means o effecting the same result; for scientific work, however, such method are, not unfrequently, employed.

Reversed Processes.—The processes we have just describe take place according to a scheme which is similar to that of th displacement of hydrogen from water by iron, only that they represen the reverse process, the displacement of a metal from its oxide b hydrogen (p. 82).

It is therefore of interest to ask whether hydrogen will not als displace the iron from iron oxide. If the previous experiment i repeated, using, however, oxide of iron in place of oxide of mercur quite similar phenomena are, as a matter of fact, observed. Wat again makes its appearance, and the oxide of iron passes into iron. This, it is true, does not look like ordinary iron, but has the appearance of a black powder. This, however, is due only to the fact that the melting point of iron is much higher than the temperature which is reached in the bulb; the iron particles, therefore, cannot unite to a coherent mass. If, however, after cooling, the contents of the bulb are taken out and rubbed with a smooth, hard object, the metallic lustre and the grey colour of iron are seen.

The interaction between iron and aqueous vapour can, therefore, be reversed, and if we write a chemical equation in the form

$$\text{Iron} + \text{water vapour} = \text{iron oxide} + \text{hydrogen},$$

t can be read in *both* directions, the substances on the left being apable of being converted into those on the right, as well as onversely. Indeed, more exact investigations have shown that both of these opposed reactions can take place at the same temperature.

The Chemical "Forces."—Such a behaviour is contradictory to he notions about "displacement," indicated on p. 84.

In the sense of this theory, the force between iron and oxygen nust, according to the experiment described on p. 82, be greater than hat between hydrogen and oxygen, because iron decomposes the ater. Conversely, according to the experiment on p. 98, the force etween hydrogen and oxygen is greater than that between iron and xygen, because hydrogen decomposes the oxide of iron.

Since it is impossible for both propositions to be correct at the ame time, it follows that the theory which leads to these propositions ust be false.

Mass Action.—As a matter of fact, the investigation of this and similar cases has shown that not only the nature and, say, the temperature are the determining factors for the occurrence of a chemical ocess, but also *the ratio of the substances present to the given volume* or e *concentration*, as well. In the present case, the water vapour acts n the iron till a certain amount of it has been converted into ydrogen, and a definite ratio between the hydrogen and the water apour obtains. Conversely, iron oxide is decomposed by hydrogen d a definite ratio is established between the hydrogen remaining and e newly formed water vapour, a ratio which is *the same as that oduced by the reverse method.*

A mixture of hydrogen and water vapour corresponding to this io acts neither on iron nor on iron oxide. The ratio is, moreover, o dependent on the temperature.

The two apparently opposed experiments of p. 82 and p. 98 proed as follows:—If iron is heated in water vapour a portion of the ter is decomposed, and a corresponding amount of iron oxide formed. e gas mixture, on being cooled in the pneumatic trough, loses the water vapour it contains, which separates out in the liquid state, and only hydrogen is collected. This is the experiment of p. 82.

On the other hand, if hydrogen be conducted over hot iron oxide, a portion of it combines with the oxygen of the latter to form water; another portion of the hydrogen remains unchanged. On passing the mixture through the colder part of the bulb-tube the water separates out as a liquid and becomes visible; the remaining hydrogen escapes unnoticed. In this way the notion arises that in both cases entirely opposite reactions take place.

Chemical Equilibrium.—Where two opposite processes mutually limit one another the state is called one of *chemical equilibrium*. Whereas formerly the view was held that such a thing occurs only in exceptional cases, there is now reason to assume that all chemical processes lead to an equilibrium. In many cases of chemical equilibrium, however, the concentrations of some of the reacting substances, corresponding to equilibrium, are so small as to escape the ordinary means of detection. The impression is then produced as if the reaction took place only in one direction.

A long historical development lies buried in the statement, that at a given temperature chemical equilibrium is determined by the *concentrations* of the reacting substances. For, although the fact that the quantity relations of the reacting substances exercise an important influence on the chemical equilibrium had been already known for over a hundred years, it was a very long time before the correct form was found for the law which obtains here. From the usual name, mass action, one might conclude that the mass or amount of the reacting substances is the determining factor; this, however, is not the case.

Let us now suppose a state of equilibrium established under given conditions between the substances just considered—iron, iron oxide, hydrogen, and aqueous vapour. Push, now, a partition into the vessel in which the above substances are contained, so that a part of the mixed gases is shut off from contact with the solid substances; no change in the equilibrium can be thereby produced. For the gases were in equilibrium with one another and with the solid substances, and equilibrium in a uniformly filled space occurs at every point, and cannot, therefore, be dependent on the size of the space filled. By the separation here imagined, however, the *absolute* amount of the gases in equilibrium with the solid substances is changed. The absolute amounts cannot, therefore, be determinative for the equilibrium.

By the separation the gases present have been separated *in the same proportions*, since they were uniformly distributed through the whole space; otherwise no equilibrium would have taken place. It is, therefore, the *relative amounts*, or the ratio of the amount, of the gases that determine the equilibrium.

The simplest and most appropriate expression for the quantity relations is got, not by representing them by the non-essential, absolute amounts, but by the amounts present *in unit volume*, or the *concentrations* of the gases or vapours present. This is the expression which we chose to start with, and we again see from this example of what importance the proper choice of magnitudes is, by which we express the laws of nature. In fact, the development of the theory of chemical equilibrium has shown itself to depend on the fact that the concentration (formerly called *active amount*) was introduced as the determining factor after various unsuccessful attempts had been made to find the suitable expression.

Influence of Solid Substances on Chemical Equilibrium.—The theorem includes as well the special law that *the amount of solid substances has no influence on chemical equilibrium.* For the concentration of solid substances, *i.e.* the ratio of amount to volume, can scarcely change; both the pressure and the temperature change this volume to such a small extent that it is of no account for the present purposes.

For the equilibrium between iron, aqueous vapour, hydrogen, and iron oxide, it is, accordingly, quite indifferent how much of the two solid substances, iron and iron oxide, is present, and in what proportions they are present.

At first sight this law appears somewhat strange, and was formerly, indeed, occasionally held in doubt. One can convince oneself, however, of the necessity of such a law by the same course of reasoning as we have just employed in the case of the gaseous portion; if equilibrium has once been established, it cannot be altered by a spatial separation of any one part of the system which is in equilibrium from the other.

Moreover, we have already met with more simple cases of the same law. The equilibrium between water and ice, or generally, between a solid substance and its fused form at the temperature of fusion, is likewise independent of the amount in which the two forms are present together. The same holds for the equilibrium between a liquid and its vapour, and likewise, also, in the somewhat more complicated case of the equilibrium between a solution and the solid substance with which the solution is saturated.

For all these single laws we can put forward the general expression, that *for equilibrium between different portions of the same system the absolute amounts of these portions are of no account, but only the concentrations within the separate portions.*

The Oxyhydrogen Flame.—The large amount of heat set free in the combustion of hydrogen causes the temperature of the hydrogen flame to reach a high point. In the case of combustion in air the temperature does not rise so high, since the heat is distributed over the admixtures in the air (p. 63). Much higher temperatures are obtained on burning hydrogen in *pure* oxygen.

The combustion may suitably take place in the *Daniell burner* (Fig.

36). This consists of two tubes placed one within the other, the mouth of one being placed behind that of the other. By means of suitable connections and taps hydrogen may be led into the annular space between the tubes, and oxygen into the inner tube. If hydrogen alone be first allowed to pass in, it burns with the usual pale blue flame at the expense of the surrounding air. A platinum wire held in the flame becomes white hot, showing that even this flame is fairly hot; the wire, however, does not melt. If the oxygen tap be now opened the flame becomes smaller and brighter, and at the same time a hissing noise is heard. If a platinum wire be now brought into the flame it immediately melts with scintillation. A watch spring immediately becomes white hot and burns with brilliant scintillations. Quartz, felspar, and similar fire-resisting minerals, melt to glassy masses.

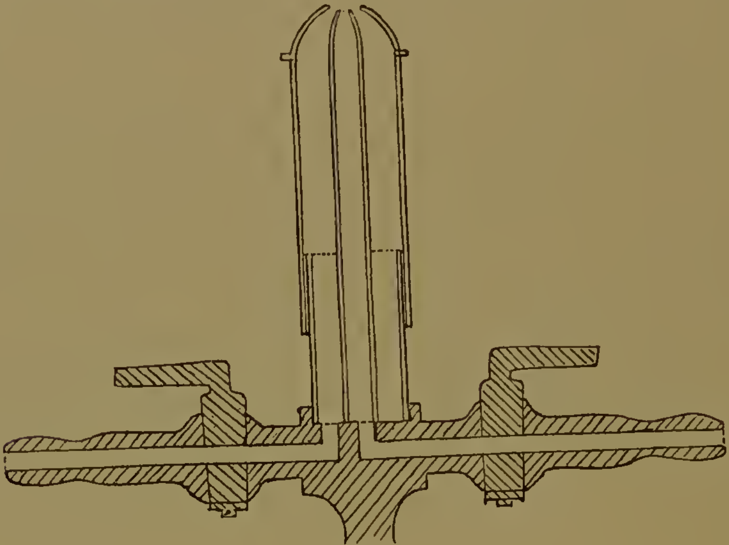

FIG. 36.

The temperature of this flame, which can be estimated at 2000°, is so high that only a few substances can withstand it without melting. One of these few substances is lime. If a piece of it be held in the flame it becomes white hot, and emits a dazzlingly bright light. Not until it has been heated a considerable time does the spot struck by the flame show signs of superficial melting (sintering).

The oxyhydrogen flame is therefore used for the purpose both of melting difficultly fusible substances and of obtaining a bright light. For this first purpose it is employed especially for melting platinum; the lime-light is used chiefly for projection purposes with the magic lantern. For the latter purpose it is convenient to use the gases compressed into steel cylinders under a pressure of a hundred atmospheres, in which form they have for some time been placed on the market (Fig. 37).

Detonating Gas.—The Daniell burner is so arranged that the two gases can only mix immediately before they are burned. If it be attempted to previously mix oxygen and hydrogen, so as to be able to burn them from a single tube, it is found that the whole stock of mixed gases instantly takes fire and combines with a loud report, the vessel usually being shattered. This explosion is very violent, and with somewhat larger quantities becomes dangerous. One must, therefore, avoid inflaming mixtures of hydrogen and oxygen without taking suitable precautions. Such mixtures, called detonating gas, are always formed when a freshly charged hydrogen apparatus, which is partially filled with air, is put in use. If the gas which is first evolved be collected in small tubes and brought into contact with a flame, the first samples behave like air and exhibit no special phenomena. Soon a gas is obtained which takes fire with a whistling noise, the flame rushing into the tube. These phenomena first become more marked and then weaker, and, at length, when all the air has been driven out of the apparatus, the gas burns quietly just as pure hydrogen does.

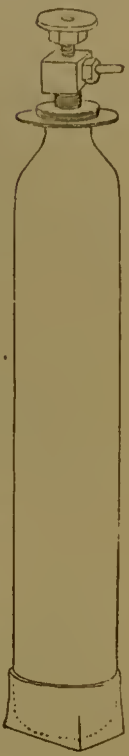
FIG. 37.

On account of the danger of an explosion, one must never omit to test in the above manner the hydrogen taken from a generator or gas-holder which has stood some time, to see if it explodes. Should it explode, the gas must be allowed to stream for some time out of the generator until a sample in a small tube is shown, by its combustion, to be pure. The contents of a gas-holder must, without fail, be rejected if they have assumed explosive properties.

The characteristic property of the explosive mixture is seen very clearly by preparing a mixture of two volumes of hydrogen and one of oxygen, and passing it into soap-water, so that a froth of bubbles filled with the explosive mixture is formed. If this froth be set on fire (after the rest of the mixture has been removed) it burns with a report like the shot of a gun.

Further Particulars concerning the Combustion of Detonating Gas.—While at comparatively high temperatures the combination of hydrogen and oxygen takes place with great violence, the two gases can be left in contact with one another at room temperature for a very long time without chemical action taking place between them.

This behaviour changes when certain metals are introduced into the gas mixture, and in this respect platinum (p. 59) is the most effective. If a piece of pure platinum foil be allowed to project into a tube containing the explosive mixture standing over water, the volume of the gas quickly diminishes, and in certain circumstances the platinum becomes so warm, owing to the heat of combination, that it glows and causes the explosion of the mixture.

Since the platinum foil, being a solid substance, can act only at its surface, its effect increases as the surface is enlarged. Platinum can be obtained, by means of chemical reactions, in a finely divided, spongy state. Such spongy platinum very quickly becomes incandescent in the explosive mixture and causes an explosion.

To moderate the reaction, the spongy platinum, in the form of a powder, is mixed with clay and formed into balls. The mass acted on by the heat produced is thereby increased and the temperature kept lower; these balls, therefore, effect a fairly rapid formation of water from the mixture of oxygen and hydrogen, but not ignition. An apparatus in which this phenomenon can be well shown is represented in Fig. 38.

Many other metals act in the same way as platinum, most of them, however, only at a somewhat higher temperature.

The platinum, and no less the other metals, undergoes no change during this action. Also, a given small quantity of platinum can convert unlimited amounts of the explosive mixture to water; the action of the platinum, therefore, does not, as in the case of a chemical combination, take place in definite proportions, but is independent of the relation between the amounts of the gas mixture and the platinum.

Reactions of this kind occur very frequently in chemistry. Not only can other gas-mixtures be caused to enter into chemical reaction by means of platinum and other metals, but liquid and gaseous substances also can exert such actions in liquids and gases; by means of these, chemical reactions which do not or do not appreciably take place without them proceed rapidly, and the acting substances can cause unlimited amounts of the other substances to react.

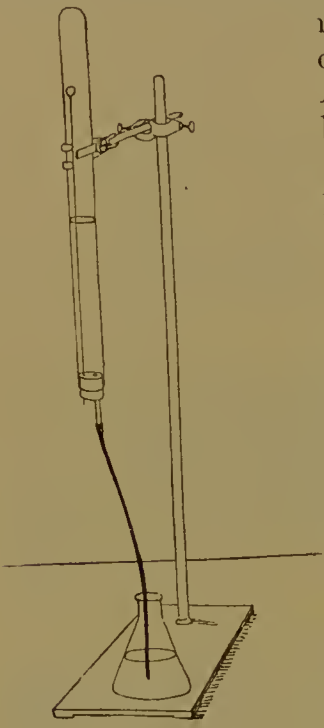

FIG. 38.

Catalysis.—For the sake of having a short designation for these important phenomena, we shall call actions of this kind *catalytic.* The substance, through the presence of which the action takes place without itself passing into the products of the reaction, is called the *catalytic substance* or *catalyser*. The process itself is called *catalysis*.

To gain an understanding of these phenomena we recall the consideration put forward on p. 64, according to which innumerable substances, between which chemical reactions could occur, can remain in contact with one another without our being able to detect such actions

At that time it was explained, that the most appropriate interpretation of these facts is that in all such cases the possible chemical reactions do, as a matter of fact, take place, but to such a small extent or with such slowness that they cannot be detected in a measurable time.

The following shows that this view is quite compatible with the universal experience. By time measurements of the progress of many chemical reactions, the approximate rule has been obtained that the velocity of chemical reactions is, on an average, doubled by a rise of 10° in the temperature. That is to say, if a reaction at a given temperature requires, say, a quarter of an hour to reach a certain point, at a temperature 10° higher it would require only 7½ minutes, and at one 10° lower 30 minutes. If the temperature is lowered 100° a $2^{10} = 1024$ times longer period is necessary, or in our example, about 11 days. On descending farther 50° or, on the whole, only the moderate amount of 150°, it would be a year before the reaction had proceeded so far as it had done in a quarter of an hour at the higher temperature.

It agrees, therefore, very well with general experience, to regard the possible chemical reactions in the cases mentioned as actually occurring, and escaping detection only through their very small velocity. So also the height of a hill or the form of a coast appears to us as something definite and unchangeable, although we know that every hill is unceasingly becoming lower, by the gradual falling down of the material of which it consists into the valley, and that every coast is changing its shape under the action of the waves.

Substances by whose presence slowly occurring reactions are accelerated re designated as positive catalysers. Since we are dealing here only with hanges in the velocity of reactions which would take place in any ase, these catalytic actions lose to a great extent the quality of unexpectedness which at first sight they appear to have.[1]

To obtain a picture of the way in which a catalyser acts, imagine a vheel-work in which the axles move with great friction, as a result, ay, of the oil having become thick, and which therefore runs down nly very slowly. If a little fresh oil be placed on the axles the vheel-work forthwith runs down much more quickly, although the vailable tension of the spring (which corresponds to the work available from the chemical reaction) is in no way altered by the oil. The ction of a catalyser may be compared with that of the oil in this espect, and also with respect to the fact that the oil is not used up in cting.

We shall soon have an opportunity of studying other peculiarities f catalytic actions.

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[1] Besides the positive catalysers or accelerators, negative catalysers or retarders are so known.

CHAPTER VII

WATER

General.—The product of the interaction of oxygen and hydrogen, or the compound of these two elements, has shown itself, in all investigations of this point which have been made, to be identical with the water which we find so very widely distributed in nature. In accordance with the law of the identity of the properties in all specimens of a given substance, we may proceed to a scientific investigation of water with that which occurs ready formed in nature, without having first to prepare it for this purpose from its two elements.

Water is one of the most widely distributed substances in nature. Not only are $\frac{4}{5}$ths of the earth's surface covered with liquid water, but our atmosphere also contains enormous quantities of water in the gaseous state, and in the polar regions and mountain heights solid water takes an essential share in the structure of the earth's surface. In addition to this the solid portion of the earth's surface is everywhere permeated with water; water is indispensable for the building-up of the vegetable and animal structures, and where organic life is seen there also is water present.

Preparation of Pure Water.—Naturally occurring water is never quite pure, since it always comes into contact with other substances and partially dissolves them. The preparation of "absolutely" pure water is an impossibility, for the very reason that one cannot exclude vessels of some kind, some portions of which can always be dissolved. On the other hand, it is not a matter of very great difficulty to prepare a water which, towards most tests, behaves as pure.

The method most used for obtaining such a water is to convert it temporarily into vapour. The impurities present in natural water are, for the most part, not measurably volatile at the temperature of boiling water, 100°, and therefore remain behind when the water is converted into vapour. Some occasional impurities, however (especially ammonia and carbonic acid), are more volatile than water; they pass over, therefore, almost entirely with the first portions of the vapour.

From this there follows the method to be employed. Water, contained in a suitable vessel, is caused to boil, and the vapours are so cooled that the condensed water can be collected apart. If, when volatile impurities are present, the first portions are rejected, a water is obtained which, for the great majority of purposes, may be regarded as pure.

This process is called *distillation*. It is employed not only for the preparation of pure water, but is also applied to many other preparations, so that the retort, the apparatus which was formerly most largely used for this purpose, has become the symbol for chemistry.

The arrangement of a distilling apparatus depends on the special purpose for which it is to be used, and especially on the amount of liquid to be distilled. In the laboratory retorts and flasks are used for small quantities.

The former are vessels with elongated necks bent lownwards. They are isually made of glass, but etorts made of other naterial are also used for pecial purposes. The apours are conducted hrough the neck into a flask pushed over it, the receiver, and re there liquefied. Since the receiver becomes strongly heated by he heat of the vapour, care must be taken to keep it cool. A imple arrangement of this kind is shown in Fig. 39.

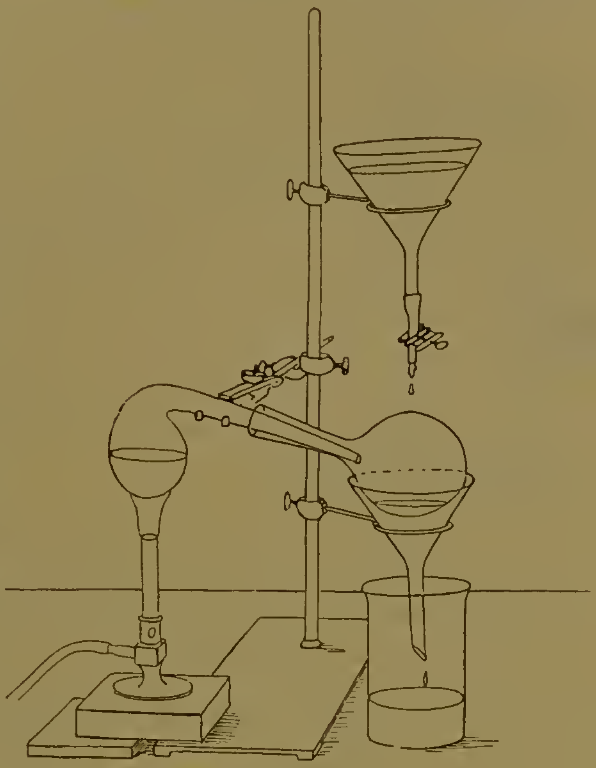
Fig. 39.

More frequently, especially where corks may be used, and in cases vhere the temperature of the vapours has to be measured, flasks vith a side tube (Fig. 40) are used for distillation. The condensation f the vapours takes place in a condenser, which has usually the form f two tubes placed one inside the other. The vapours are passed nto the inner tube, and into the space between the two tubes water is llowed to flow, which absorbs the heat of the vapours. To make the est use of the water, it is allowed to enter at the foot and to pass pwards in a direction opposite to that of the vapour. In this way he water may pass almost boiling hot out of the upper end of the ondenser, while at the lower end the distillate is completely cooled.

The *principle of counter currents* applied here, which allows of the most economical use of the acting substances, is applied to an exceedingly large extent in chemical apparatus, and will be repeatedly met with.

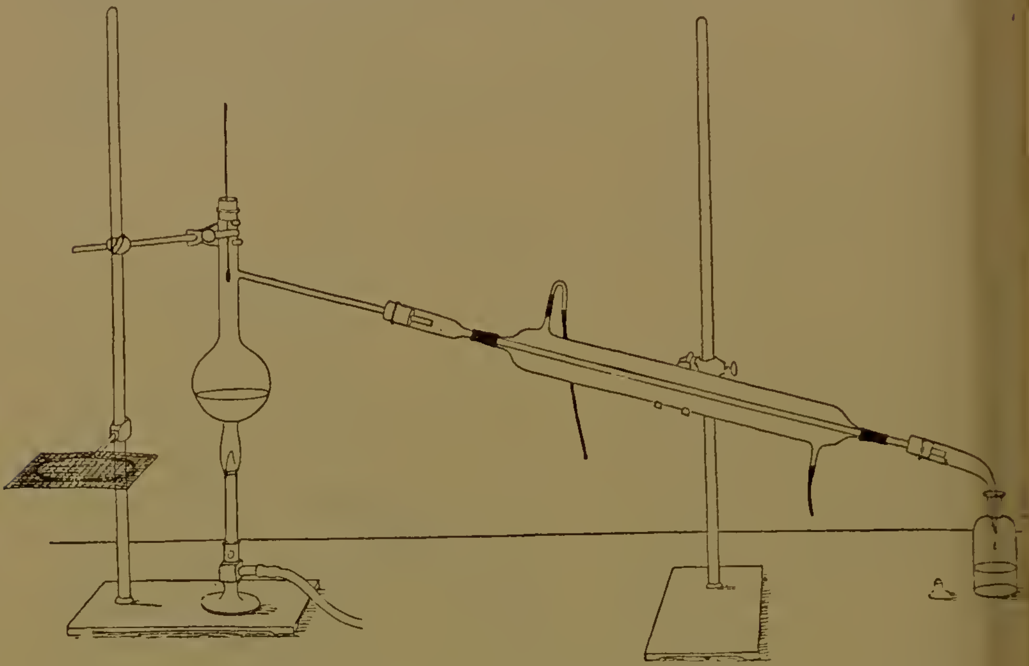

Fig. 40.

Such apparatus are sufficient for liquids of a few litres in amount.

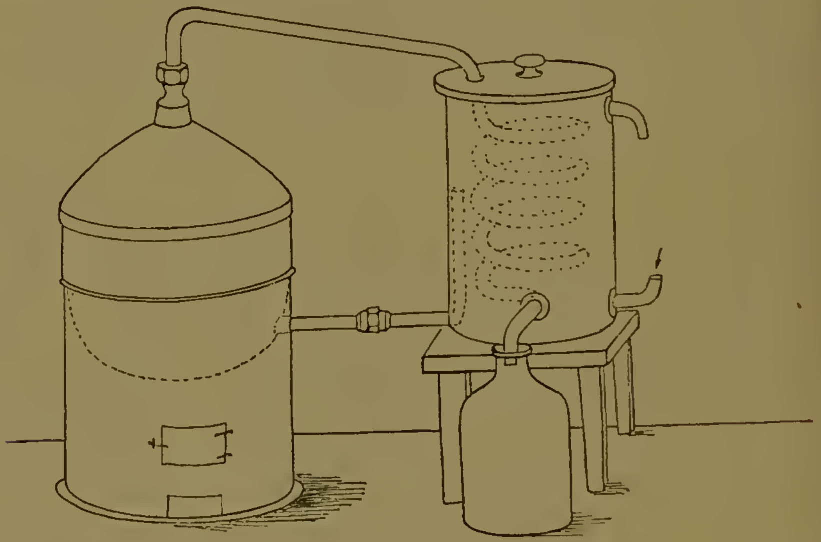

Fig. 41.

Where larger amounts are dealt with, such as in the preparation of distilled water for the purposes of a large laboratory, the distilling vessel, or "still," is made of metal, generally of copper. The condenser has the form of a tube bent round like a screw, and is made of pure tin, because this metal is practically not attacked by water. It stands n a larger vessel through which water is allowed to flow, in this case also from below upwards. The warm water which passes out at the op may be suitably used for feeding the still, so as to recover a part of the heat. Such an apparatus is represented in Fig. 41.

To demonstrate the effect of distillation, a quantity of water is coloured with ink and distilled from an apparatus, such as is shown in Fig. 39 or 40. The water passes over colourless and tasteless.

Properties—Colour.—At ordinary temperatures water is a transparent, colourless liquid. This absence of colour, however, is only apparent; in thick layers water exhibits a distinct, fine blue coloration, which is peculiar to pure water and is not in any way due to admixtures. The blue coloration is produced owing to the fact that water absorbs yellow and red rays, *i.e.* converts them into heat; when these are withdrawn from white light the complementary colour, blue, remains. This blue colour is seen in lakes and seas containing very pure water; in most cases of naturally occurring water it is masked by the presence of coloured admixtures.

Density.—As has already been mentioned, the density of water has been made equal to unity, the unit of mass, 1 gm., having been ascribed to the unit volume 1 cc. of water. This number, however, holds only for the definite temperature 4°, since the density of water, ike that of all other substances, changes with the temperature.

In the case of water this change occurs in a manner essentially different from that in the case of other substances. On heating water rom 0° upwards the density does not *decrease*, as is usually the case, but it *increases*. At 4° water attains its maximum density, and this is he reason why this temperature has been chosen for the definition of unit density. From 4° onwards the density of water, as of all other ubstances, decreases with rising temperature, and at 100° amounts to bout $\frac{1}{24}$th less than at 0°. The extensity, or the specific volume, behaves in the reverse manner; it has its smallest value at 4°, and at ll other temperatures its value is greater.

The following table gives a summary of the relation between the emperature and the density and extensity of water:—

	d	e
0°	0·999874	1·000127
4°	1·000000	1·000000
10°	0·999736	1·000265
20°	0·998252	1·001751
30°	0·995705	1·004314
40°	0·99233	1·00773
50°	0·98813	1·01201
60°	0·98331	1·01697
70°	0·97790	1·02260
80°	0·97191	1·02890
90°	0·96550	1·03574
100°	0·95863	1·04315

The same relation can be represented by the geometrical method described on p. 73, the temperatures being taken as abscissæ, and the extensity as ordinates. In this way we obtain Fig. 42, which represents the relation of the volume to the temperature.

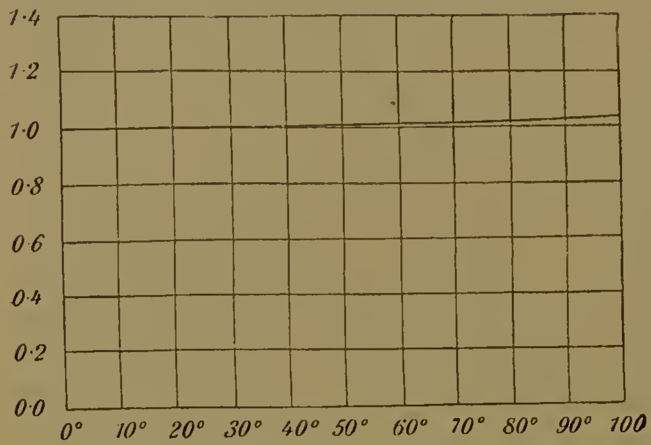

Fig. 42.

The decrease in the extensity between 0° and 4° is so small that it cannot be represented in the figure. It would cause a lowering of the curve by only $\frac{1}{400}$th mm. To represent it the scale of temperatures, as well as that of volumes, must be considerably increased. A suitable diagram would be obtained by taking the temperatures ten times, and the volumes a thousand times, as great. Our drawing would, however, thereby become much too large. If, however, we examine Fig. 42 with regard to that portion which interests us just now, we notice that there is a large empty space between the curve and the base-line. We can leave this out, and instead of the base-line corresponding to the volume zero, we can choose another near the curve itself. For such a purpose it is well to choose a line corresponding to the volume 1·0000. On this line the temperatures are marked off on a scale ten times larger than before. Perpendicular to it there are marked off, not the volumes themselves, but only their differences from the value 1·0000.

In this way Fig. 43 is obtained. To render the measurement easier the whole field is divided by a rectangular network. In a manner which is readily intelligible, the numerals placed at the edges allow of the extensity corresponding to each temperature, and *vice versa*, being read off. The figure is repeated only up to 10°.

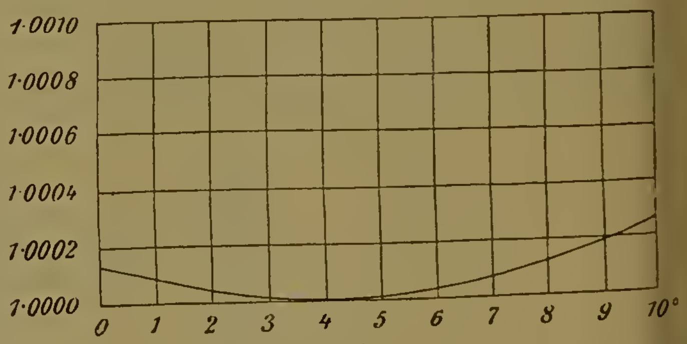

Fig. 43.

The Law of Continuity.—In the table on p. 109, only the densities and volumes corresponding to certain definite temperatures are given. The question now arises as to how the intermediate values, for which there are no data, can be ascertained. For this purpose use is made of a general law, the application of which is so familiar to us that it appears axiomatic, although, like all the other laws of nature, it is a summary of manifold experience.

The law in question is called the law of *continuity*, and is to the following effect:—When two magnitudes change simultaneously with one another, so that for a definite value of the one there is also always a definite value of the other, *the simultaneous changes always remain proportional.* When, therefore, the one magnitude is allowed to increase continuously, the other also increases continuously, and if the one change is made smaller and smaller till it becomes zero, the change of the other magnitude also becomes zero.

It follows from this that when two (not too remote) values A_1 and A_2 of the first magnitude are given, to which there correspond the values B_1 and B_2 of the second, the values of B, corresponding to values intermediate between A_1 and A_2, lie between B_1 and B_2.

If the values A_1 and A_2 are sufficiently close, one may even assume a *proportionality* between the two series of values. If A_x is a value intermediate between A_1 and A_2, and B_x the corresponding value of the other magnitude, we may write the following equation:—

$$\frac{A_1 - A_x}{A_1 - A_2} = \frac{B_1 - B_x}{B_1 - B_2}$$

rom which we find B_x to be,

$$B_x = B_1 - \frac{B_1 - B_2}{A_1 - A_2}(A_1 - A_x).$$

This formula allows of the calculation of intermediate values which have not been determined, from the measured values on either ide of them. It is all the more exact the closer the measured values re to one another. If in any given case it is not exact enough, it an be replaced by a more complicated formula, which also depends on he principle of continuity, which, however, will not be deduced here.

The process which we have just described is called *interpolation.* The method will be familiar to the reader from the use of logarithm ables, where the values of the logarithms or numbers not given in the ables are obtained from the adjacent ones by means of such a calcu- ation by proportion.

It lies in the nature of what we have just been considering, that he method can be used only for obtaining intermediate values, and may by no means be extended beyond the region of measurement. uch a method, *extrapolation*, is applicable, at most, only in closest roximity to the last point measured, and readily leads to errors if extended more widely. Such errors due to extrapolation are not unfrequently found in science (p. 75).

It must further be mentioned that although, in nature, continuous processes form the rule, interrupted ones are not excluded. These, however, are always easily recognised, since when one property changes discontinuously most of the others simultaneously undergo a discontinuous change, so that a general change of state which cannot be overlooked occurs.

Graphic Representation.—These remarks become very clear if the interdependence of the magnitudes be represented by a line, according to the directions on p. 73. Only single points of such a line can be determined experimentally, and the intermediate parts are, to start with, unknown. The law of continuity, however, entitles us to join these single points by a continuous line, passing without break or fluctuation through the points determined by measurement. This line then represents the desired relation for all intermediate values of the variable magnitudes, and replaces the interpolation formula given on p. 111.

The graphic representation is, in many cases, to be preferred to calculation. Interpolation by calculation, which presupposes *proportional* changes of the two magnitudes, is represented graphically by the assumption that the line between the points employed is straight. Even for curved lines this is so much the less removed from the truth the more closely the points are chosen, as can be immediately seen from a glance at Fig. 44. If, however, the points are rather farther apart, it is much easier to make the path of the line approach the truth by the graphic method than by calculation, which in this case is rather complicated.

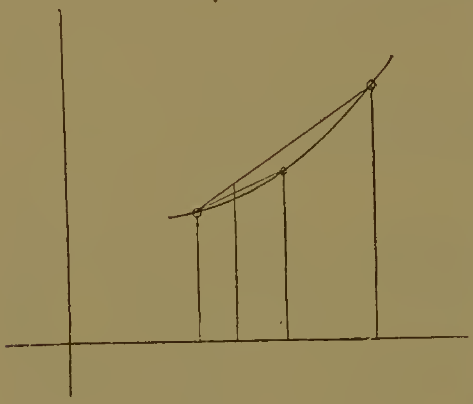

Fig. 44.

Other cases of such interdependence may be treated in the same way, if the general law is known which connects the magnitudes. Thus, the calculation of the influence of the pressure and the temperature in the case of gases, would not be more simple by the use of the formula $pv = r\mathrm{T}$ for each single case than interpolation from a table or reading off from a curve. For the expansion of water by heat, however, such a general formula is not known, and interpolation or a curve is therefore the only aid to its representation.

The Coefficient of Expansion.—The ratio between the change of the extensity and that of the temperature is called the *coefficient of expansion*. In the case of gases this is independent of the temperature.

ince, of course, the graduation of the scale of temperature was defined n such a manner that the degrees were made proportional to the xpansion. For every degree, therefore, the volume increased by the ame amount. In the case of water it is otherwise. Below 4° the xpansion is negative; that is to say, as the temperature rises the olume becomes smaller. This continues to 4°; beyond this the oefficient of expansion becomes positive. It does not, however, etain its numerical value unchanged, but the ratio of the two changes, r the increase of volume pro degree continually increases.

These peculiarities are pictured in the curve in an easily intelli-ible manner. So long as the coefficient of expansion is negative the urve sinks downwards to the base-line; the positive coefficient onditions an ascending of the curve. The fact that the coefficient ncreases with rising temperature produces a curvature with the onvex side downwards; if it decreased with rising temperature the urve would be concave on the under side. A straight line would e the criterion of a coefficient which did not depend on the tem-erature.

In this way, when, for some still unknown relation between two agnitudes, a few corresponding pairs of values have been determined y measurement, a curve can be drawn, and from its form important formation as to the nature of the relation can be obtained.

The coefficient of expansion has already been defined as the ratio the increase of the extensity with the temperature. In the case of ses, where the coefficient is independent of the temperature, this finition causes no difficulty in the practical measurement. It is only cessary to measure the volumes corresponding to any two tempera-res, and the value sought is obtained by dividing the one difference the other. The result is all the more exact the larger the interval, cause the experimental error is divided by a correspondingly greater visor, and its influence therefore rendered smaller.

The case is different where the coefficients of expansion are riable. In this case different values are obtained not only at ferent temperatures, but also when, starting from the same nperature, the coefficient is determined between varying intervals.

A distinction is therefore made between the mean and the true fficient. The former is defined with regard to a definite range of nperature, and is obtained by dividing the difference of volume by difference of temperature. It represents the value which the fficient of expansion would have if the expansion in that region re uniform.

The true coefficient of expansion cannot, on account of its varia-ty, be determined by direct measurement. It may be looked upon he ratio between infinitely small changes of volume and tempera-e; these, however, cannot be measured. It can be obtained by a thematical operation known as differentiation, when the relation between the two magnitudes is known in the form of an algebraic formula.

These considerations can be explained in geometrical form by Fig. 45. If ac represents the change of temperature and cb that of the volume, cb/ac is equal to the mean coefficient of expansion between a and c. To determine the true coefficient of expansion for the point a, the point b would have to be moved infinitely near to a. The secant ab then becomes the tangent ae. The true coefficient of expansion, therefore, for a definite temperature is obtained by drawing a tangent at the corresponding point of the curve. The ratio of the two increments ce/ac, determined by this straight line, gives the numerical value of the true coefficient of expansion at the point a.

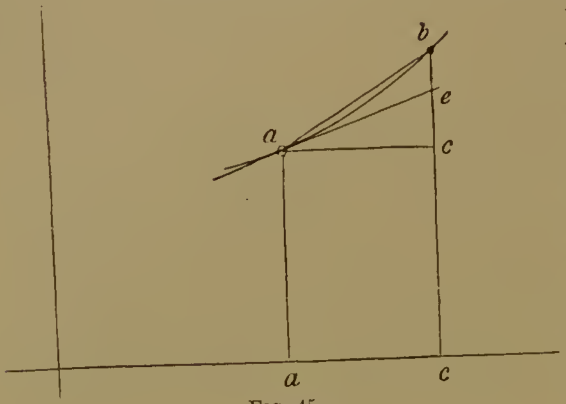

Fig. 45.

It follows from this that at 4° the coefficient of expansion o water is zero, for the tangent at the lowest point of the curve i horizontal, and indicates, therefore, no increase at all. In the neighbourhood of 4° the coefficient of expansion is not zero, but is ver small. The error in the density, corresponding to a given temperatur error, is therefore smaller in this region than anywhere else. Thi remark is of importance for the derivation of the unit of mass fror the unit of volume, by means of water at 4°.

The Degrees of Freedom of Liquid Water.—The volume water can be affected by change of pressure as well as by change temperature. This variability is, however, still smaller than that du to the temperature. At 20° the coefficient of compressibility of wat is equal to 0·000046, *i.e.* 1 cc. of water decreases in volume b 0·000046 cc. when subjected to a pressure of one atmospher This number depends, in a rather complicated manner, on tl temperature, as can be seen from the following table :—

Coefficient of Compressibility of Water.

0°	$51·77 \times 10^{-6}$	60°	$41·15 \times 10^{-6}$
10°	48·54 ,,	62°	41·12 ,,
20°	46·09 ,,	70°	41·19 ,,
30°	44·14 ,,	80°	41·51 ,,
40°	42·65 ,,	90°	42·11 ,,
50°	41·68 ,,	100°	43·00 ,,

In general, liquid water, and likewise every other simple liqu varies, with respect to pressure, temperature, and volume, in the sa general fashion as a gas (p. 72). At any time only *two* of these magnitudes can be independently fixed; the third is then no longer undetermined. Liquids have, therefore, as many degrees of freedom as gases, viz., two.

We can immediately extend this principle to the case of solid substances. In this case also the volume varies with the temperature and pressure, although still less than in the case of liquids; if, however, both are fixed the volume is also completely determined.

We can therefore lay down the general principle, that *every simple body*—solid, liquid, or gaseous—*possesses two degrees of freedom with respect to its cubic and thermic variability.* As we shall soon see, the number of the degrees of freedom diminishes when we are dealing with a substance in several physical states, instead of with a uniform body.

Ice.—At 0° water passes from the liquid into the solid state and is converted into ice. So long as water and ice are present together their temperature is always 0°. The absolute or the relative amounts of the two forms or "phases" have no influence. This is the reason why this temperature, which is easily obtained and can be maintained unchanged for any length of time, has been chosen as a fundamental point in thermometry.

This temperature, however, is produced exactly only when the water is pure. If it contains foreign substances of any kind in solution, the temperature at which the solution is in equilibrium with ice is lower. The ice which freezes out from such a solution, however, is pure; for this reason, ice obtained from ordinary river or sea water exhibits the correct melting point, and the formation and separation of ice from impure water is a method of obtaining pure water.

Properties of Ice.—Ice is a transparent substance of a bluish olour which, in comparatively thick layers, *e.g.* in the fissures of glaciers, appears as a fine, pure blue. Its density is considerably less han that of water at the same temperature, for at 0° it is only 0·91674 as compared with that of water, 0·99987. Conversely, the xtensity is greater, being equal to 1·09083 as compared with 1·00013 n the case of water; 1 cc. of water, therefore, on freezing, increases n volume by 0·09070 cc., *i.e.* by about $\frac{1}{11}$th.

In this respect water forms an exception to the usual behaviour of ubstances on freezing, whereby a diminution of the volume or increase f the density almost always occurs. For this reason ice floats on ater, whereas other solid substances sink in their melts.

Ice is a *crystalline* substance, *i.e.* a substance whose properties vary a regular manner with the direction in the piece. The most conicuous consequence of this variation with the direction is the outward rm which such a substance assumes when it is allowed to pass into e solid state undisturbed by outward influence. This is, however, no means the only peculiarity of this kind; on the contrary, all properties in crystals which can vary at all with the direction are dependent on this.

In contradistinction to the crystalline substances which possess the peculiarity just mentioned, there are the *amorphous* substances in which that peculiarity is not present. Glass, for example, is an amorphous substance. Two rods, cut in any directions out of a larger piece of glass, behave in all respects identically when they have the same shape. On the other hand, two rods of ice, one of which is cut, say, parallel, the other perpendicular to the face of a naturally formed sheet, behave differently; for example, one breaks much more easily than the other.

The crystalline nature is seen most clearly in ice which has been able to assume its shape undisturbed. Thus, the ice on the surface of freezing masses of water first forms in long needles, joined to one another at an angle of 60°, and the ice flowers on window-panes are likewise an expression of the crystalline nature of ice.

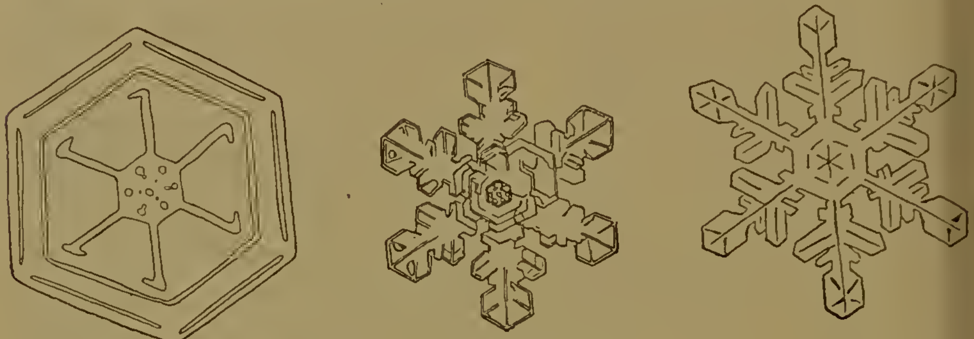

FIG. 46.

The crystals, however, of which snow consists, can form in the least disturbed manner, for they form floating in the air. As a rule, certainly, these crystals are small and indistinct; under certain circumstances, however, they grow so large that they can be seen with the naked eye. They then usually appear as flat stars, developed according to a 2 × 3-fold symmetry. Some snow crystals are shown in Fig. 46.

The property of occurring in crystalline shape is a very wide spread peculiarity of solid substances, and the formation of crystals may generally be denoted as a property of pure substances. The amorphous state, on the other hand, is confined almost entirely to mixtures. The crystalline form is an important characteristic o solid substances, and we shall repeatedly have an opportunity o discussing these relations later.

Supercooling.—The formation of ice in water which has been cooled to 0° does not necessarily occur. On the contrary, with som care, water can be cooled to several degrees below zero without i becoming solid. At the same time it retains the peculiarity of expanding as the temperature sinks.

Water in this condition is called *supercooled.* It solidifies immediately on being touched with a piece of ice, its temperature thereby rising to 0°. If preserved from contact with ice, it can be kept any length of time in the liquid state if it is only supercooled a few degrees. If, however, the supercooling is carried further, solidification takes place spontaneously without the presence of ready-formed ice.

The condition of supercooled water has often been compared with that of unstable equilibrium in mechanics; the comparison, however, does not prove correct. A body in unstable equilibrium seeks a new position so soon as it experiences the smallest displacement; supercooled water, however, can withstand disturbances of the most varied kind without solidifying, and responds only on contact with ice. The region of supercooling nearest to the melting point is therefore designated as *metastable,* and only the more remote regions, in which solidification takes place spontaneously, are called unstable.

Heat of Fusion and Solidification.—When water solidifies heat is developed. For this reason partially solidified water still retains the temperature 0°, even when the surrounding temperature is lower, for as heat is withdrawn it is supplied anew by the solidification of fresh amounts of water. Conversely, ice absorbs heat on melting; for this reason, a mixture of ice and water in warmer surroundings does not become warmer, for the heat which enters the mixture is used up in melting ice.

The amount of heat absorbed in fusion is equal to that set free by the solidification of the same quantity of water. This is a necessary consequence of the law of conservation of energy, for if there were a difference between the two, one could, by causing water to alternately solidify and melt, create or destroy as much heat as one wished, without the water being used up or undergoing any permanent change.

Unit of Heat.—To express this amount of heat numerically, a *unit of heat* must, first of all, be fixed. This can best be done if we ecall the fact that heat, being a form of energy, can be obtained from work or kinetic energy, and *vice versa.* The natural unit of heat is, accordingly, the amount of heat which can be obtained from the unit of work or of kinetic energy, the *erg* (p. 23).

Quantities of heat, however, had been measured long before the elation between work and heat was known. As the unit of quantity of heat there was employed that amount which is required to heat one gram of water one degree. This amount is called the small calorie, bbreviated cal. A more suitable unit than this one, which varies omewhat with the temperature, and also contains the difficulty to which the division of the fundamental interval between the freezing nd the boiling point of water is subject, is the rational calorie, K;

this represents the amount of heat required to heat one gram of water from the melting to the boiling point. It is pretty nearly equal to a hundred times the small calorie; 100 cal. = 1 K.

Through the fundamental investigations of Mayer and of Joule (1842-43), the relation between the units of work and heat were ascertained, and the numerical value of this has been established with great exactness by Joule's and later measurements. The result of these is that one small calorie at 18° is equal to 41,800,000 erg. In technical work the amount 10,000,000 erg is much used, and is called a joule; a small calorie is, therefore, equal to 4·18 joule, or 1 cal. = 4·18 *j*. A rational calorie is a hundred times as great: 1 K = 418 *j*.

If the amount of heat required to melt 1 gm. of ice be measured it is found to be 80 cal. If, therefore, 80 gm. of water at 1° be mixed with 1 gm. of ice at 0°, the temperature of the whole, after the fusion of the ice, will be exactly 0°. This amount, 80 cal., or 334 *j*, is called the heat of fusion or the latent heat of ice.

Application of Ice.—Numerous technical and scientific applications of ice are due to the circumstance that it absorbs such a large amount of heat on melting. Thus it is used for preserving meat and other food-substances, the harmful processes of decomposition, which cause the meat to become bad, being at the temperature of 0° hindered or at least greatly retarded. Its application in science depends on the constancy of its temperature of fusion; even large spaces can, with its help, be kept for any length of time at the unvarying temperature of 0°, and phenomena, therefore, which are dependent on the temperature can be observed without disturbance from that side. Thus, for example, the very exact comparisons of the standard metre measures are carried out in melting ice.

If ice be brought together with salt, or with similar readily soluble substances, a solution is produced, the freezing point of which is much lower than that of ice, and the temperature sinks considerably under 0°; it sinks to the temperature of the freezing point of the solution produced. This phenomenon conditions the application of ice to *freezing mixtures*. With ordinary common salt a temperature as low as − 18° can be obtained by using three parts of ice to one part of salt.

Another application of the same phenomenon is the melting of snow by means of salt, which is employed as an expeditious means of freeing tramway lines from snow.

The Transition of Water into the Gaseous State.—If water or ice be brought into a given space, which is empty or which contains a gas, in such an amount that the space is not completely filled by it part of the water passes into the gaseous state. This takes place at all temperatures, although to a varying degree. The law which obtains here states that evaporation goes on until the vapours have assumed a definite density, which is dependent only on the temperature

On the other hand, it is independent of the amount of non-gaseous water, of the volume, and also of the presence of other gases in the space.[1]

This law is generally stated in such a way that there is attributed to the water vapour a definite *pressure* which is dependent only on the temperature. Since pressure and density are related to one another, the second form of statement is essentially the same as the first; and since, as a rule, pressure is more easily measured than the density of the vapour, most measurements are referred to the pressure. In the case, however, of evaporation in a space filled with a gas, we must not reckon with the total pressure, but only with the partial pressure of the vapour.

To demonstrate this last phenomenon, a small sealed bulb containing some readily volatile substance (*e.g.* ether) is introduced into a closed bottle furnished with a mercury manometer (a tube bent like a U and filled with mercury, Fig. 47). After the pressure has been observed the small bulb is broken. The pressure then increases by an amount equal to the vapour pressure of the liquid at the existing temperature.

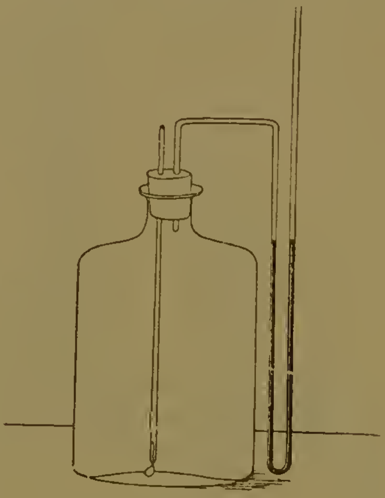
Fig. 47.

The phenomenon we are dealing with here is one of equilibrium in the sense discussed on p. 100. At a given temperature, water vapour alone can exist both at smaller as well also as at greater values of density and pressure than when in contact with liquid water. If, however, it comes in contact with water it cannot retain its state. In the first case water will evaporate, in the second, vapour will condense, and this will go on ntil the *concentration* or the *density* and the pressure have reached the alue corresponding to the existing temperature.

This kind of equilibrium obeys exactly the same laws as chemical quilibrium in the narrower sense. It is best, therefore, to place the eciprocal changes of the physical state of the same substance alongide of the ordinary chemical processes, and to regard them as the implest examples of that kind. Indeed, the criterion of chemical ransformations, the change in the properties of the substance, is ound in this case also. It is only the great readiness and simplicity ith which these processes occur, both forwards and backwards, that ave caused the superfluous separation of these phenomena from the hemical, as being "physical" changes of state (p. 7).

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[1] Strictly speaking, the last circumstance has, certainly, an influence, but it is uite negligible in those cases where the gas is not absorbed in large quantities by e liquid water.

The dependence of the vapour pressure of water on the temperature is shown in the following table and in Fig. 48. By reason of their special importance the pressures in the regions between 10° and 25°, as also in the neighbourhood of the boiling point, are given in greater detail in two further tables.

Vapour Pressure of Water.

– 19°	0·1029 cm.	30°	3·151 cm.	80°	35·49 cm.
– 10°	0·2151 ,,	40°	5·49 ,,	90°	52·55 ,,
+ 0°	0·4569 ,,	50°	9·20 ,,	100°	76·00 ,,
10°	0·9140 ,,	60°	14·89 ,,	110°	107·5 ,,
20°	1·7363 ,,	70°	23·33 ,,		

10° – 25°

10°	0·914 cm.
11°	0·977 ,,
12°	1·043 ,,
13°	1·114 ,,
14°	1·188 ,,
15°	1·267 ,,
16°	1·351 ,,
17°	1·439 ,,
18°	1·533 ,,
19°	1·632 ,,
20°	1·736 ,,
21°	1·847 ,,
22°	1·963 ,,
23°	2·086 ,,
24°	2·215 ,,
25°	2·352 ,,

90° – 100°

90°	52·55 cm.
91°	54·58 ,,
92°	56·67 ,,
93°	58·83 ,,
94°	61·06 ,,
95°	63·37 ,,
96°	65·74 ,,
97°	68·19 ,,
98°	70·71 ,,
99°	73·32 ,,
100°	76·00 ,,

Boiling.—The boiling point of water is the temperature at which its vapour pressure is equal to the external pressure. If water be heated, say, by a flame, its temperature can rise only to this point; all further heat which is communicated to it is used up in the formation of vapour, which escapes in bubbles from the water. One must not say, therefore, that the boiling point is that temperature at which water forms vapour, for vapour is formed at all temperatures. The formation of bubbles of vapour, however, within the liquid is not possible till the boiling point is reached.

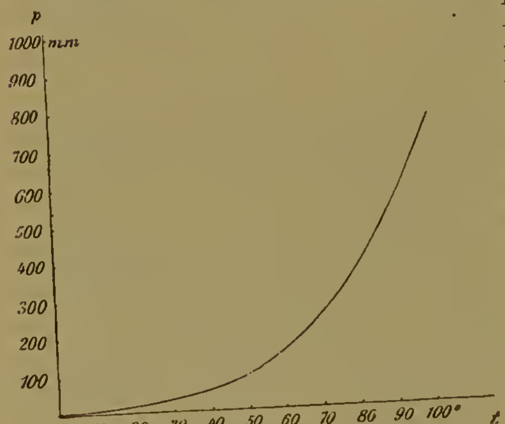

FIG. 48.

A liquid, like water, can therefore boil at very different temperatures; a special boiling point corresponds to each pressure:—This fact can be shown by means of the following experiment. Water is heated to boiling in a round-bottomed flask. When the vapour streams out copiously the flask is closed with a good-fitting cork, and is at the same time removed from the source of heat. Although now the water is constantly losing heat by radiation, it still continues boiling. When boiling has ceased it can be again caused to commence by pouring cold water over the flask.

The explanation of this apparent contradiction, that water can be made to boil by cooling, lies in the fact that the cooling affects the small quantity of vapour much more than the large amount of water. The vapour condenses on the cooled walls of the vessel, and the internal pressure is thereby so much lowered that the water, which has remained warmer, must again boil.

The correctness of this explanation can be shown with the apparatus in Fig. 49. The boiling flask is closed by a cork carrying a tube bent twice at right angles. The outer limb of this tube must be about 80 cm. long; it dips into a vessel with mercury. The water is made to boil until the air is all driven out of the flask; this is known by the crackling noise produced by the condensation of the water vapour in the mercury. The flame is then removed and the same observations can be made as before. Every time that cold water is poured over the flask the mercury in the tube rushes upwards, and indicates the diminution of pressure; at the same time the water begins to boil, and the mercury again sinks, but not to its former position.

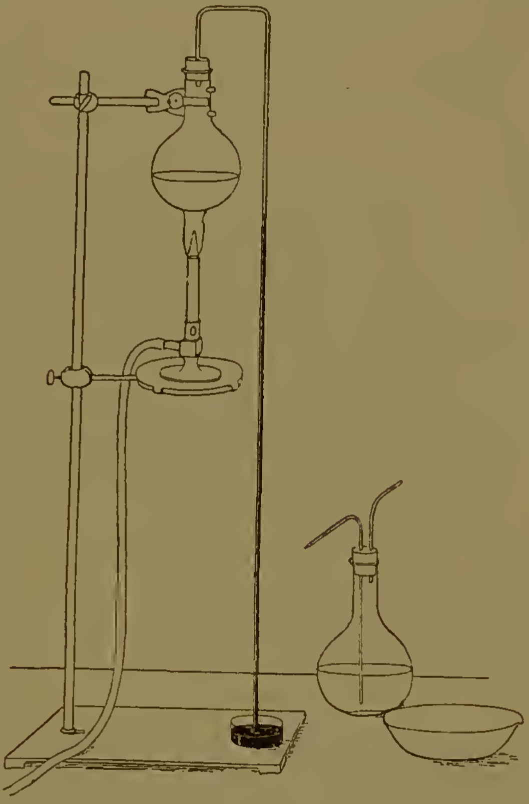

Fig. 49.

As the temperature falls the vapour pressure becomes smaller, but at 0° it still amounts to 0·4 cm. mercury. Ice, which is in equilibrium with water at this temperature, has the same vapour pressure. Even below 0° ice has a measurable vapour pressure, which becomes smaller the more the temperature sinks. Whether there is a temperature above the absolute zero at which the vapour pressure of ice is, in all strictness, equal to zero, cannot be established with certainty; probably there is not.

If the pressure is increased above one atmosphere the boiling point rises. Under two atmospheres it is at 121°; under ten atmospheres, at 180°. At the same time the vapour becomes denser, while the density of the water, corresponding to the increase of temperature, diminishes. We must therefore ultimately reach a temperature and a pressure at which the density of the vapour becomes equal to that of the water. At this point water and vapour have become identical, and a phenomenon similar to boiling can now no longer occur. This point is called the critical point. In the case of water it lies at about 200 atmospheres' pressure and 365°; these values, however, cannot be determined with exactness, since under these conditions water strongly attacks the vessels, especially glass.

Density and Extensity of Water Vapour.—The vapours of volatile liquids possess a density and extensity as well as the ordinary gases. But the circumstance that vapours frequently cannot be observed under normal conditions, *i.e.* under a pressure of 76 cm. mercury and at 0°, since under these conditions they pass into liquids, calls for some remarks.

Since, however, vapours, so long as they remain in the gaseous state, likewise obey the gas laws,[1] the density and specific volume are calculated on the supposition that the vapours would remain gaseous also under normal conditions, and would behave according to the gas laws. This is done for the purpose of retaining the advantage of comparison with the gases. By choosing the pressure of 0·1 cm. as normal pressure, the normal condition could be made a practicable one for many vapours, including the vapour of water; this would, however, not be the case for all substances. No disadvantage, however, arises by employing the usual calculation, since in using it we are always dealing only with an arithmetical relation.

Measurements of the density of water vapour have shown it to be 0·0008045, calculated for the normal conditions, and its extensity 1243 cc. In other words, 1 cc. of water vapour at 0°, and under a pressure of 76 cm., would weigh 0·0008045 gm., and 1 gm. would occupy the volume 1243 cc.

For chemical purposes it is better to refer the densities to the normal gas, defined on p. 88, *i.e.* we calculate the molar weight of water vapour. This is found, by dividing the absolute density of water vapour by that of the normal gas (0·00004466), to be 18·02.

The Water Vapour in the Air.—Water in the form of vapour is contained in the atmospheric air, but by no means in so large amount as it could be. In view of the distribution of water on the earth's surface, one might expect that the air would contain as much water vapour mixed with it as corresponds to the vapour pressure at the prevailing temperature. If, however, a determination be made, it is found that the air is not "saturated" with water vapour, but contains, on an average, only three-fourths of this amount. The amount varies with the state of the weather, and one speaks, therefore, of moist or dry air. Still, air which is called moist scarcely ever contains as much water vapour as it could contain, and air which is called dry may contain as much as half the maximum amount.

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[1] Vapours, like gases, deviate from the simple gas laws when their density exceeds a definite value. The point at which this occurs, it is true, usually makes its appearance sooner in the case of vapours than in the case of gases. It is dependent on the nature of the substance.

The cause of this lies in the great variableness of the vapour pressure with the temperature, as is seen from the table on p. 120. If, at one point, the air has taken up as much water vapour as corresponds to the vapour pressure, and it reaches a place where it becomes warmer, it becomes unsaturated, *i.e.* the concentration of water vapour in it is smaller than corresponds to the equilibrium. On the other hand, if the air falls to a lower temperature, part of the water separates out in the liquid or solid form, as dew, rain, or snow, and on being heated again to its former temperature the air is again unsaturated. The differences of temperature, therefore, at the earth's surface continually act so that the air contains less water vapour than corresponds to its temperature, and for this reason our atmosphere is never completely saturated with water vapour.

The presence of aqueous vapour in the air is so far of importance to the chemist that all objects exposed to the air take up more or less water. Not only do substances which are soluble in water, such as salt and sugar, become moist in air containing water, but also insoluble substances, such as glass, stones, metals, textile fabrics, become covered with a thin film of water, which must, when necessary, be taken into account. The amount of water taken up depends on the nature of the substance, and is, for the rest, proportional to the surface. Bodies with a large surface, powders and cellular structures, such as are produced in plants, take up a specially large amount of water corresponding to their large surface.

* This water does not have the properties of liquid water. Not only does the object not feel wet, but the *vapour pressure* of this surface-held water also is lower than that of liquid water at the same temperature, and it is all the lower the smaller the amount of water on a given surface.

In many cases it is necessary to remove this water. For example, to obtain the exact weight of a body in powder, it must be weighed without its film of water. The most simple means of freeing the body from this consists in heating it to redness, for, as the temperature rises, the vapour pressure of the surface water also increases, and the latter escapes into the relatively dry, hot air. If, however, it is not possible to raise the temperature of the body, it is dried by being placed in dry air. For this purpose glass apparatus, called desiccators, are used, Fig. 50. They contain a substance which combines with water and withdraws this from the air. Into this dry air there again evaporates water from the substance to be dried, and this process goes on until the vapour pressure of the water on the substance has become as small as that of the water combined with the desiccating substance.

Some such desiccating substances have been previously mentioned (p. 87); others will be mentioned as occasion serves.

Since the drying process, as above described, depends on the movement of the water vapour from the body to the drying substance, it will take place all the quicker the more rapid this movement is. If, therefore, we fill the desiccator with hydrogen instead of with air, the body will dry more quickly, because the diffusion of the aqueous vapour takes place more quickly through the lighter hydrogen than through the heavier air. The drying, however, proceeds most quickly when the desiccator is evacuated, because the movement of the aqueous vapour then takes place without any hindrance. It would be a mistake to suppose that the substance could be brought to a higher degree of dryness in an exhausted desiccator than in one containing air; for the vapour pressure is the same whether air is present or not. The whole difference is one of rapidity, and in a given limited time a substance would certainly become drier in an evacuated desiccator than in one containing air.

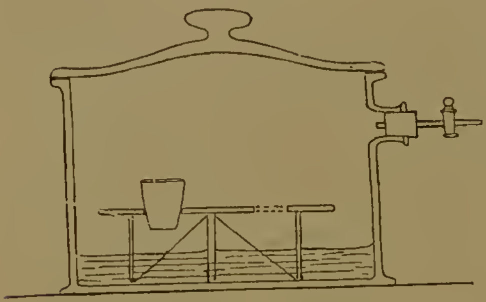

FIG. 50.

We must also take into consideration here, that as the body becomes drier its vapour pressure diminishes. Since, now, the passage of the vapour to the desiccating substance takes place all the more quickly the greater the concentration of the water vapour, there lies a retarding factor in the progress of the drying itself, and the further advanced the desiccation is, so much the more slowly is the remainder of the water removed. This is a universal phenomenon. When any state of equilibrium strives to establish itself with a certain velocity, this velocity diminishes in the same measure as the state of equilibrium is approached, for, in general, the velocity of every process is proportional to its distance from the position of equilibrium.

Among other things it follows from this, that, strictly speaking, every state of equilibrium will be reached only after an infinitely long time. Since, however, our means of measurement are of limited accuracy, a state is in many cases reached, even after a short time, which, practically, cannot be distinguished from the state of equilibrium.

On the other hand, it is important to know that there is no *absolutely* drying substance. Every substance which takes up water can also give up water, and drying substances are merely substances which give off water with a very small pressure. In this sense sulphuric acid is a better drying agent than calcium chloride.

The Heat of Evaporation of Water.—On the passage of water into vapour heat is absorbed, and this in much larger amount than in the transition of ice to liquid water. This consumption of heat is usually attributed to the circumstance that on passing into vapour the particles of water are separated from one another. But when water passes into ice the particles are also separated from one another, since ice is $\frac{1}{11}$th less dense, and still this transition is accompanied, not by an absorption, but by a development of heat. It is best, therefore, to free oneself entirely from such hypotheses. Since the differences between the different states of the same substance are, ultimately, always reducible to differences in the energies present, a passing out or in of energy naturally accompanies the passage from one state to another, and the fact, as such, requires no "explanation." All that science has to do here is limited to the exact measurement of the phenomenon, and to establishing its relations with other existing conditions.

The general law may now be enunciated, that with every transition from the solid to the liquid, and from the liquid to the gaseous state, there is joined a consumption of energy, which is generally absorbed in the form of heat. No exception is known to this law, and only at the critical point, where the difference of states disappears, does the difference of energy also become zero.

For the conversion of 1 gm. of water at 100° into vapour at the same temperature, 537 cal., or 2245 *j* are required. The same amount of heat becomes free when vapour at 100° is converted into water at the same temperature. This amount is called the latent heat of water vapour, or the heat of vaporisation.

The value of the heat of vaporisation is dependent on the temperature at which the vaporisation is effected. Since, at the critical point, it becomes zero, it must decrease with rising temperature; its value, however, is not known up to this point. For the purpose of calculating the work performed by steam-engines, the value, within small limits, has been often determined. It is represented by the formula $606{\cdot}5 - 0{\cdot}695t$ cal., or $2535 - 2{\cdot}905t\ j$.

The large amount of heat which becomes free on the condensation of steam affords a convenient means of transporting heat, without, at the same time, having to convey much substance. When steam is generated in a boiler, conveyed away through tubes, and condensed at another place, this process is equivalent to the transportation of a corresponding amount of heat. If it were wished to accomplish the same transport of heat by means of hot water, at least five times as great a weight would be required. For this reason steam finds manifold application for heating and warming purposes, and in addition to this, it has the peculiarity which is frequently very valuable, that under atmospheric pressure the temperature cannot rise above 100°.

The last property is also made use of in the laboratory for water and steam baths. These are used for maintaining apparatus at temperatures not exceeding 100°, a thing which is necessary in cases where a higher temperature would be detrimental to the heated substance or apparatus. Such a bath usually consists of a metal boiling vessel above which there is a space for the vapour. To enable objects of different sizes to be placed upon it the lid consists either of a single plate, furnished with openings of various sizes, or of a series of concentric rings placed one within the other (Fig. 51). To be able to set the bath quickly in action it is an advantage that it should contain very little water. Since, however, this small amount of water would soon boil away, a water-supply is arranged to replace the loss. This consists either of a Mariotte's bottle, which maintains the level of the water in the bath at a definite height, or an overflow can be attached to the boiler (Fig. 52); by taking care to have a supply of water from the main in excess of the consumption in the boiler the same result is obtained.

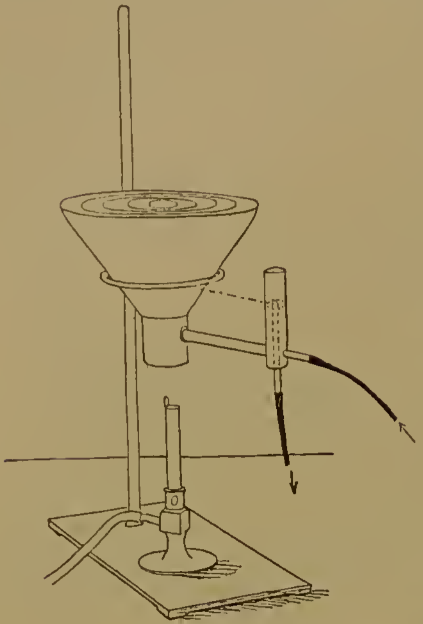

FIG. 51.

Another property of steam, of which much use is made in the laboratory, is the constancy of its temperature. If a receptacle be fixed into the boiler so that the steam surrounds, but cannot penetrate into it, one possesses, so long as the water in the boiler is in ebullition, a space in which the temperature remains constantly at 100°. This is the most convenient means of obtaining a constant fairly high temperature, such as is necessary for the performance of many chemical and physical investigations.

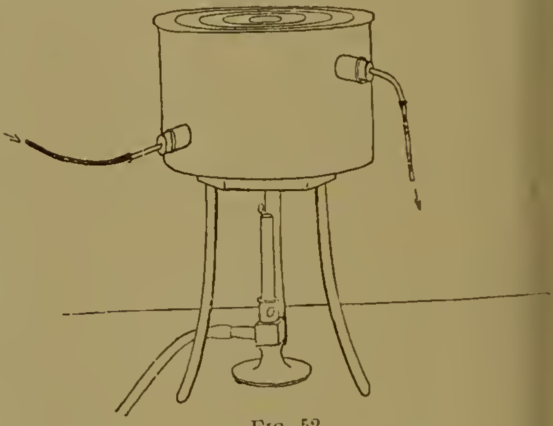

FIG. 52.

The boiling point of water, certainly, varies somewhat with the pressure; the variation amounts to 0·037° for every millimetre of mercury. From this one can see whether, in any given case, the height of the barometer must be taken into account or not.

Superheated Water and Overcooled Vapour.—Just as it is possible to lower the temperature of water below its freezing point, if the precaution is taken that no ready-formed ice is present (p. 116), so water may be heated above its boiling point when the presence of vapour is excluded, and vapour may be cooled below its point of condensation when the presence of liquid water is excluded.[1]

The first experiment can be performed in various ways. If linseed oil be heated to over 100°, and small drops of water, which has been previously boiled (to expel the dissolved air), be introduced into the oil, the temperature can, with some care, be raised to 130°-140°, at which the vapour pressure would amount to 2·7 and 3·6 atmospheres respectively, without the formation of vapour taking place. On raising the temperature still higher a copious formation of vapour suddenly takes place with explosion.

The same phenomenon is observed if water be kept boiling some time in a glass vessel which has been made as clean as possible by washing out with a solution of caustic soda and sulphuric acid. The phenomenon of "bumping" then occurs, *i.e.* ebullition does not occur for some time, and then begins suddenly, accompanied by an excessive evolution of vapour. The reason that the water is "superheated" lies in the fact that, by the cleansing of the surface and the long boiling, the air-bubbles have been removed, which, as a rule, adhere to points here and there on the vessel; at these the formation of vapour readily takes place because some vapour is already present. If these "nuclei" are removed superheating occurs; and when at length the first bubble of vapour is produced, all the heat absorbed above 100° serves to form vapour, a large amount of which is thereby suddenly developed.

Such cases of superheating occur also with other liquids. It can be avoided by taking care that some bubbles of air are always present within the liquid. For this purpose porous substances of all kinds are used, in which air is contained, or such substances as under the existing conditions evolve traces of gas.[2]

Superheating sometimes also occurs on a large scale. It is, for example, one of the causes of boiler explosions.

The other case, that vapours, in the absence of liquids (or solids, which have the same effect), can be subjected to pressures which are greater than the pressure of condensation, can also be obtained experimentally. When the air in a large bottle containing air and some water, so that the air is saturated with water vapour, is rarefied, a lowering of temperature is thereby produced. This is due to the fact that the expanding air performs work, and since this is not communicated to it in the form of other work, the air must yield it up in the form of heat; it must, therefore, become colder. At the same time, the vapour which is present is thereby cooled and reduced to a temperature at which the ordinary vapour pressure is smaller than the existing partial pressure of the aqueous vapour.

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[1] One would also expect that it would be possible to heat ice above its melting point if the presence of water is excluded. Although no well-ground objection can be made to this, it must be mentioned that such an overstepping has never been successful either in the case of water or of any other substance. Presumably, it is exceedingly difficult to exclude the liquid form.

[2] It is chiefly causes of a similar kind which effect the acceleration of the evolution of oxygen from fused potassium chlorate (p. 62).

If the experiment is performed immediately after the apparatus has been put together, the result of the cooling of the vapour is seen; the latter is precipitated in the form of a mist. The mist can be seen with especial distinctness by allowing a ray of light to pass through the vessel.

If, however, the apparatus is allowed to remain at rest for 24 hours the experiment is no longer successful, and on exhaustion the interior remains clear. This is due to the fact that all the dust particles in the air of the apparatus have fallen down. The over-cooled vapour does not find any "nuclei" on which it can condense, and it therefore retains its vaporous form.

We can therefore state the principle generally, that the definite relation between pressure and temperature in the case of aqueous vapour (and in the case of the vapours of all other liquids) is valid only so long as vapour and liquid are *simultaneously* present. So soon as one of these two forms is wanting the point can be overstepped from either side.

Phases and Degrees of Freedom.—Whereas, therefore, water alone, and likewise vapour alone, possess two degrees of freedom for the variations of their pressure, volume, and temperature (pp. 73 and 115), there remains only *one* degree of freedom left when vapour and liquid are *simultaneously* present, for, in that case, only the pressure *or* the temperature can be arbitrarily fixed. If a pressure has been chosen, this can exist only at a definite temperature, and, likewise, any chosen temperature only at a definite pressure.

The question, how the matter then stands in the case of the *volume*, can be answered to the effect that, in this case, the volume has no influence on the pressure or temperature. For if we have vapour and liquid given (*e.g.* at 100° and under atmospheric pressure in the case of water), the volume may be increased or diminished without variation of pressure or temperature; only so much water is converted into vapour, or vapour into water, that the new space is again filled with vapour and water at the same pressure.

The vapour and liquid are called two different *phases* of water. In general, those parts of a given system which have the same properties, and which can thereby be distinguished from other parts which may be present, possessing other properties, are called phases. Water and vapour are two different phases of water.

Phases are not necessarily simple substances, but they are homogeneous substances (p. 8); solutions may also appear as phases. On the other hand, mixtures of solid substances, *e.g.* granite (p. 8), contain as many phases as there are different kinds of solid substances present in the mixture, since these are distinguishable *alongside* of one another. When several phases are present they are always spatially distinct, and can be mechanically separated from one another.

The law that can be deduced from the behaviour of a system which contains the two phases vapour and liquid, is that one of the existing degrees of freedom is lost by the formation of the second phase. The condition that a second phase shall be present, must, therefore, be regarded as the disposal of one of the magnitudes which can be arbitrarily changed, and, accordingly, *the number of degrees of freedom diminishes in proportion as the number of the phases increases.*

Influence of Pressure on the Melting Point of Ice.—An application of the relations which have just been deduced can be at once made to the system ice-water. The temperature at which both exist side by side has been given as constant (p. 115). We are dealing here with one substance in two phases, water and ice, and we must therefore conclude that here also one degree of freedom still exists, as in the case of the system, water and vapour, *i.e.* that different temperatures also correspond to different pressures.

The theoretical conclusion that such a variability must exist led investigation to the actual discovery of the variability, which was not previously known. It was found that the melting point of ice sinks as the pressure increases.

This variability is, certainly, very small, for it amounts to only 0·0073° for one atmosphere. To produce a change in the melting point of 1° a pressure of 136 atmospheres is necessary.

The small changes to which the atmospheric pressure is subject, and which may be estimated at $\frac{1}{10}$th of an atmosphere, alter, therefore, he melting point of ice at most by 0·0007°, *i.e.* by an amount which can scarcely be detected even with a sensitive thermometer. They may, therefore, be neglected even in the case of exact measurements. Although the definition of the melting point has to be referred to a definite pressure, that of one atmosphere, there is, in practice, scarcely ever occasion to take the influence of pressure into account.

By very high pressure, therefore, water can be prevented from freezing in the cold of winter. Thus water was enclosed in a steel vessel, and by the rattling of a ball enclosed along with the water, it was ascertained that the latter still remained liquid at −20°. The requisite pressure had been established automatically by the freezing of a little water. Since ice has a volume $\frac{1}{11}$th greater than that of water, the solidification of a small amount in the closed space is ufficient to produce a very considerable pressure.

* This peculiarity of ice of melting under pressure has a great influence on the meteorological and geographical properties of solid water. When two pieces of ice are pressed against one another they melt at the surface of pressure; the issuing water which escapes from

the pressure forthwith solidifies again, and the two pieces of ice are thus joined together to a whole. This is the cause that loose snow forms coherent masses when it is pressed. As every one knows from making snowballs, this cohering of the snow occurs all the more readily the nearer its temperature is to the melting point; the reason of this is clear from what goes before.

* The same peculiarity brings it about that the snow on the tops of high mountains gradually passes into *névés*. It also effects the remarkable phenomenon of the flowing of glaciers. As is known, these ice-masses move slowly downwards from the heights of the mountains to the valleys, as if they consisted of a semi-fluid mass. This is due to the fact, that at all parts where the ice-mass rests on the ground a liquefaction takes place at those points which are under the greatest pressure, and this causes a sliding. The ice behaves like a slide-way with automatic greasing, and so sets itself in motion under its own pressure.

* It is easy to convince oneself of this property by pressing lumps of ice together in suitable moulds. Even when the temperature is carefully kept below zero the lumps unite to form clear masses of ice, which fill out the moulds like a metal cast.

All liquids do not behave like water; in the case of almost all the melting point becomes higher and not lower with increase of pressure. The difference lies in the fact that water, as contrasted with other liquids, expands on solidification. Substances which have a smaller volume in the solid state than in the liquid exhibit a rise in the melting point with pressure.

States of Equilibrium — Law of Reaction.—The relation between the change of volume on solidification and the shifting of the point of solidification with the pressure is not a chance one, but is a necessity. It is a case of a universal law that holds for all states of equilibrium. It can be expressed as follows: *If a system in equilibrium is subjected to a constraint by which the equilibrium is shifted, a reaction takes place which opposes the constraint, i.e. one by which its effect is partially destroyed.*

Apply this principle, now, to the present case, in which we have a mixture of ice and water at 0° in equilibrium. If we exercise a pressure on the mixture by diminishing its volume the equilibrium is disturbed, and a process must occur by which the pressure is again partially relieved, *i.e.* by which a diminution in volume is produced. This consists in ice melting, for liquid water occupies a smaller space than the ice from which it is produced. The melting point of ice must, therefore, sink with pressure.

If, on the other hand, the volume diminishes on solidification, this latter must be brought about by increase of pressure, *i.e.* the melting point rises with the pressure.

The foundation of the above-stated universal law, which has manifold application in chemistry and physics, lies in the conception of equilibrium. By equilibrium we understand a state which tends to re-establish itself when it is disturbed. This tendency finds expression in the occurrence of phenomena which seek to reverse the disturbance, and the general expression of this tendency is the law enunciated above.

* The term equilibrium is, as is known, derived from mechanics. There it is usual to distinguish three kinds of equilibrium: stable, unstable, and indifferent. In chemistry the conception of equilibrium, as is apparent from the definition just given, is applied only in the form which corresponds to *stable* equilibrium in mechanics.

The Triple Point.—On applying to water the rule just enounced, that increase of the phases runs parallel with the diminution of the degrees of freedom, we come to the conclusion that it must certainly be possible to have three phases of water side by side, but that such a system has no degrees of freedom left. It can, therefore, exist only at a definite temperature and a definite pressure.

Such a possibility does, as a matter of fact, exist when ice and water are introduced into an empty space. The space then becomes filled with aqueous vapour, and we have ice, water, and vapour side by side.

The pressure is, in this case, equal to the pressure of water at 0°, viz., 0·4 cm. mercury; the temperature is very nearly equal to 0°. It is not exactly equal to this, for 0° has been defined as the melting point of ice under atmospheric pressure; under the pressure of 0·4 cm. prevailing here, which is almost exactly one atmosphere less, the temperature is therefore + 0·0073° (p. 129). The pressure is, accordingly, a little higher, but the difference does not affect the last decimal in the number stated.

These are the only values of temperature and pressure at which the three phases of water can exist side by side, and any change of one of these values causes the disappearance of the one or other phase. If the pressure is raised, the vapour disappears; if it is lowered, the water disappears. If the temperature is raised, the ice disappears; if t is lowered, the water disappears.

Such an invariable point, in which three phases of a substance can xist side by side, is also called a *triple point*. Speaking generally, very substance will possess a triple point situated in proximity to he melting point. Since, however, the melting points are scattered ver the whole range of the measurable temperatures, so also are the riple points, and many of these are accessible only with difficulty.

Vapour Pressure of Ice.—As has been experimentally and theoretically proved, water and ice have the same vapour pressure t 0°. It amounts, as already stated, to 0·4 cm. mercury.

We may, however, ask how the vapour pressure of water cooled below 0° is related to that of ice at the same temperature. This is explained in Fig. 53. The temperature is measured on the base-line; the vapour pressure curves of the water and of the ice are denoted by *w* and *i*. At 0° the two lines cut; at that point, therefore, the vapour pressure of both forms of the substance water is the same. To the left of this is shown the vapour pressure curve of the supercooled water as an unbroken continuation of that of the warmer water; it lies above the vapour pressure curve of ice. At the same temperature, therefore, supercooled water has a greater vapour pressure than ice.

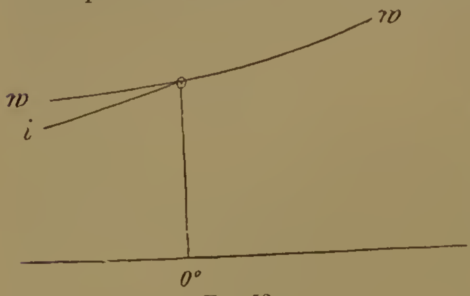

FIG. 53.

This is the reason why supercooled water cannot exist in contact with ice. Imagine a two-limbed tube, Fig. 54, filled at *w* with water and at *i* with ice. At 0° the whole will remain in rest, since the vapour pressure of ice is equal to that of water. At temperatures below zero, however, the pressure above the water is greater than that above the ice. Vapour must, therefore, be constantly given off by the water and be taken up by the ice, and this can cease only when all the water has become converted into ice.

We can now enounce the general principle: *That which is in equilibrium in one way must be in equilibrium in every way; and that which in one way is not in equilibrium can in no way be in equilibrium.* If, therefore, ice and supercooled water are not in equilibrium as regards their vapours, neither can they be in equilibrium when they are in immediate contact, and in both cases the transformation must occur in the same sense.

The principle of which we have just made use is of the greatest importance, and has a very varied application. It ranks along with the principle of the conservation of energy, and, like it, can be deduced from the impossibility of a *perpetuum mobile*. Whereas the latter principle denies the possibility of creating energy out of nothing, the former principle denies the possibility of setting in motion, for the performance of work, energy which is at rest. In this way, also, a *perpetuum mobile* would be possible, as can be readily seen from isolated examples. A steamship moves through the sea at the expense of the energy which is yielded by the burning coal: this generates kinetic energy which, by reason of friction, ultimately passes into heat. The water in the ocean, now, contains an enormous amount of heat. If it were possible to use this heat for moving the ship, it would ultimately return again as heat into the ocean, and it would not be necessary to create any energy in order to obtain a *perpetuum mobile*. That this also is an impossibility, *that a system in equilibrium*

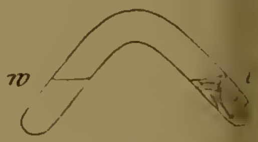

FIG. 54.

does not, spontaneously, set itself in motion, is a further independent principle obtained by experience.

A distinction is therefore drawn between a *perpetuum mobile* of the first kind, in which energy would have to be created, and a *perpetuum mobile* of the second kind, in which energy at rest would have spontaneously to set itself in motion. The impossibility of the former represents the first law of thermodynamics; the impossibility of the latter, the second law.

The manifold and important conclusions which follow from the second law will often occupy us later. In spite of its apparent simplicity, and even almost axiomatic character, it allows of results being obtained which by no means lie on the surface.

Water as Solvent.—Numerous substances form solutions, *i.e.* pass into homogeneous liquids, with water. These still exhibit essentially the physical properties of water, but also other properties, depending on the substances dissolved. The property of forming solutions is of the greatest importance in chemistry, since chemical processes occur most readily between liquid substances. The range of chemical phenomena would, therefore, be much more limited and difficult of access than it is if the formation of solutions did not occur. By this means the soluble solid bodies and gases are rendered capable of reaction, and one of the most frequent preliminaries to chemical operations consists in bringing the participating substances into solution.

The formation of aqueous solutions is not limited to solid substances such as sugar and salt, but solutions can also be yielded by liquid and gaseous substances. For the properties of the solutions produced it is indifferent in what physical state the dissolved substance previously existed. Thus, entirely identical solutions are btained when equal amounts of alcohol are added to water, one ime as liquid and the other time as vapour.

By reason of the dissolved substances the properties of water ndergo continuous modification, which is so much the greater the arger the amount of dissolved substance. The vapour pressure of ater, more especially, is always diminished by dissolved substances, nd the diminution is proportional to the dissolved amount so long as his does not exceed certain limits (in round numbers, a tenth of the eight of the water). As a rule this is joined with a rise of the oiling point; only in the case where the dissolved substance itself is olatile does it take part in the vapour pressure, and then the boiling oint may fall through the addition, although the partial pressure of he water vapour in the vapour mixture is always less than the pressure f pure water at the same temperature.

For the rest this influence obeys definite and very remarkable ws, of which we shall presently speak (Chap. VIII.).

The freezing point is quite similarly affected by dissolved substances, sinking proportionally to the amount of dissolved substance. This law also, like the foregoing one, holds only for dilute solutions.

Relations between the Changes of the Vapour Pressure and of the Freezing Point.—The phenomena of the lowering of the vapour pressure and of the freezing point, through dissolved substances, are interdependent. As was explained on p. 131, water and ice at 0° are in equilibrium, because at this temperature both have the same vapour pressure. If, now, the vapour pressure of water is diminished through the solution of a foreign substance, the solution can no longer be in equilibrium with ice at 0°, but only at a temperature at which both pressures are again equal. If, in Fig. 55, *w* represent the vapour pressure curve of liquid water and *i* that of ice, the vapour pressure curve of a solution will, according to what has been said, have the position *s*. The identity of the vapour pressures of solution and ice occurs at the point where the two curves *i* and *s* cut,—in any case, therefore, below 0°,—and this point will be so much the lower the more the vapour pressure of the solution has been diminished. A constant relation, therefore, which is independent of the nature and amount of the dissolved substance exists between the lowering of the vapour pressure and of the freezing point. Solutions which exhibit the same diminution of the vapour pressure must also exhibit the same lowering of the freezing point. Stated in numbers, the relation is such that a solution whose vapour pressure is $\frac{1}{100}$th less than that of pure water freezes 1·05° lower than pure water.

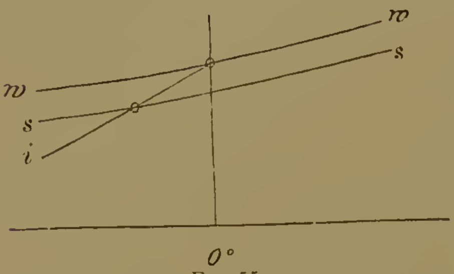

Fig. 55.

The regularities which have been set forth here in the case of aqueous solutions are not restricted to these, but are, on the contrary, universally valid for liquid solutions of every kind.

Chemical Properties of Water.—The reactions which occur by the action of water on other substances are, on the one hand, determined by the fact that it is a derivative of oxygen and hydrogen, so that it can give rise to other oxygen and hydrogen compounds. On the other hand, water can combine with substances without the elimination of one of its components. Such compounds are called *hydrates*, from the Greek name for water.

We have already become acquainted with some of the first reactions, namely, those which led to the production of hydrogen, whereby the substances added combined with the oxygen. Reactions whereby, conversely, the hydrogen is bound and the oxygen set free are also known, and will be discussed later (Chap. IX.).

The compounds produced by the taking up of both the elements of water, which are called hydrates, are very various in kind. Many of them can be again very readily resolved into their components; by a rise of temperature, especially, water is formed from them as vapour. In the case of such hydrates it is usually assumed that they contain the water "as such," in contradistinction to such compounds as do not give off water. This method of expression, however, has no definite meaning (cf. p. 39), and closer investigation shows that an unbroken transition exists between the two classes, all the hydrates being capable of being arranged in a continuous series, according to the ease with which they give off water. The measure of this readiness is the pressure of the vapour above these substances at a definite temperature. We shall enter more fully into these relations at a later point (Chap. XXI.).

Water, likewise, frequently exercises an influence on chemical reactions through its two components oxygen and hydrogen. Since, for the reasons just given (p. 133), most chemical reactions are carried out in aqueous solution, we have in all these cases the further possibility of the water also acting chemically.

This consists, essentially, in the fact that in chemical reactions the elements of water can, at the same time, leave or enter a substance. If hydrogen be conveyed to a substance containing oxygen, the latter may either take up the hydrogen, or it can also lose oxygen, which is then eliminated with the hydrogen as water. Likewise, a substance containing hydrogen can, in contact with oxygen, become either richer n oxygen or poorer in hydrogen, the oxygen in the first case being simply taken up, in the second case forming water which is eliminated.

The taking up of oxygen is called oxidation; its withdrawal, reduction. In the sense of what has just been said, however, the result of the oxidation can be a decrease of the hydrogen instead of an increase of the oxygen; in the same way, a reduction can result n an increase of the hydrogen instead of a loss of oxygen. In queous solution it is frequently not an easy matter to decide which f the two possibilities has occurred. It is, therefore, generally agreed o regard the taking up of hydrogen also as a reduction in any given ase, and the loss of hydrogen as an oxidation. We shall also continue o use these expressions in the double sense.

The Quantitative Composition of Water.—The experiments escribed on pp. 98 ff., which demonstrate the composition of water from xygen and hydrogen, can, by suitable elaboration, be used to establish uantitatively the proportions of these two elements. Two questions rise here, that of the ratio of the weights and that of the ratio of the olumes of oxygen and hydrogen.

The ratio of the weights, a knowledge of which is of importance r chemistry, was first determined with some degree of exactness by Berzelius and Dulong, 1819) in the following way:—In a glass tube there was placed a weighed quantity of oxide of copper, *i.e.* a compound of oxygen with copper, and, while being heated, pure, dry hydrogen was passed over it. Water was thereby produced, and copper remained behind in the tube and was weighed. The water was carefully collected, its last vaporous portions being retained by calcium chloride (p. 87), and likewise weighed. From this the following data were obtained :—

The weight of the oxygen in the water produced is equal to the loss in weight of the copper oxide, which has yielded up its oxygen for this purpose. The weight of the hydrogen is equal to the weight of the water produced, diminished by the weight of the oxygen contained in it, according to the law of the conservation of weight. From this the ratio is obtained in which the two elements are united to form water.

These experiments have subsequently been many times repeated and modified, and have led to the following ratio :—

Oxygen . .	0·8881
Hydrogen . .	0·1119

Since, on account of their small density, gases can, of all substances, be weighed with the least certainty, it could not be hoped, at the time of Berzelius' and Dulong's experiments, that sufficient accuracy would be attained by the direct weighing of the gases and of the water produced from them. Recently this experiment also has been performed on a large scale, and with splendid accuracy, by Morley, and has yielded a result which is in entire agreement with that cited above.

The Ratio of Oxygen to Hydrogen by Volume.—From the known ratio of the weights in which oxygen and hydrogen combine to form water, the ratio of the volumes can be obtained by multiplying the weights of the gases by their extensities, or dividing by the densities. The result of the calculation is as follows :—

1 gm. hydrogen occupies, in the normal state, the volume 11,111 cc. ; 0·1119 gm., therefore, occupies 1243 cc.

1 gm. oxygen occupies, in the normal state, the volume 699·84 cc. ; 0·8881 gm., therefore, occupies 621 cc.

The two numbers 1243 and 621, however, are exactly in the ratio 2 : 1, *i.e.* two volumes of hydrogen and one volume of oxygen unite to form one volume of water.

The question immediately arises concerning the volume ratio of the water vapour produced. From p. 122 the extensity of water vapour is found to be 1243 ; since the preceding calculation gives the volumes of the amounts of oxygen and hydrogen contained in one gm. of water, it is seen that the water vapour produced occupies, in the vaporous condition, exactly the same volume as was occupied by the hydrogen which has been used up. Altogether, therefore, the volume ratios are as follows:—

two volumes of hydrogen
and one volume of oxygen
give two volumes of aqueous vapour.

This calculation has, in the first instance, been carried out for the normal state of the three gaseous substances, *i.e.* for the pressure of one atmosphere and the temperature 0°. Since, now, the ratio of the volumes of any two quantities of gas always remains the same, however the common pressure and common temperature are altered, these relations hold also for all other pressures and temperatures; therefore they hold universally.

Decomposition of Water.—We can convince ourselves of the existence of this important relation in a clear manner, by decomposing water into its elements and measuring the volume of these. Such a decomposition of water is most easily effected with the help of the electric current. If such a current of sufficient potential and strength be passed through water, the two constituents of the water are evolved, in the form of colourless gases, at those points where the current enters and leaves the liquid. One of these gases is readily identified as oxygen, since it kindles a glowing wood-splinter. The other does not support combustion, but can be ignited in contact with the air, and burns with a pale flame; it is therefore hydrogen.

The processes in the decomposition of water by the electric current are made up of the following phenomena:—While, as is known, the current is conducted through metals without any other change taking place in the conductor than that it becomes more or less heated, there is another class of conductors which behave in an essentially different manner. In these also, it is true, a rise of temperature occurs which depends on the resistance in exactly the same way as in the case of the metallic conductors or conductors of the first class. Besides this, however, the conductors of the second class have the peculiarity that the current cannot pass in them without the substances at the same time undergoing movement, some substances moving in the direction of the current or in the direction of movement of the positive electricity, others in the opposite direction. Both movements always take place imultaneously and are, as was discovered by Faraday (1833), proporional to the strength of the current, *i.e.* to the amount of electricity vhich passes.

So long, now, as the current is passing solely within the conductor f the second class, this circumstance does not cause any noticeable differnce as compared with the processes which we know in the case of onductors of the first class. So soon, however, as the current passes rom a conductor of the second class to one of the first, in which it ows without the transportation of substance, an accumulation of the transported substances must occur at the junctions of the two conductors, and these substances separate out.

Thus, in water the hydrogen moves with the positive electricity, the oxygen with the negative. At that point, therefore, where the positive electricity passes out, the *cathode*, hydrogen appears; at the point where the positive electricity enters, or where the negative electricity passes out, the *anode*, oxygen appears.

In order to carry out the electrical decomposition, or *electrolysis*, of water, therefore, the latter must be placed between two metallic conductors which effect the passage of the current. The apparatus have different construction, according to the purpose in view. An apparatus, the purpose of which is not to allow of the most advantageous electrolysis possible, but of a convenient demonstration of the processes, is represented in Fig. 56.

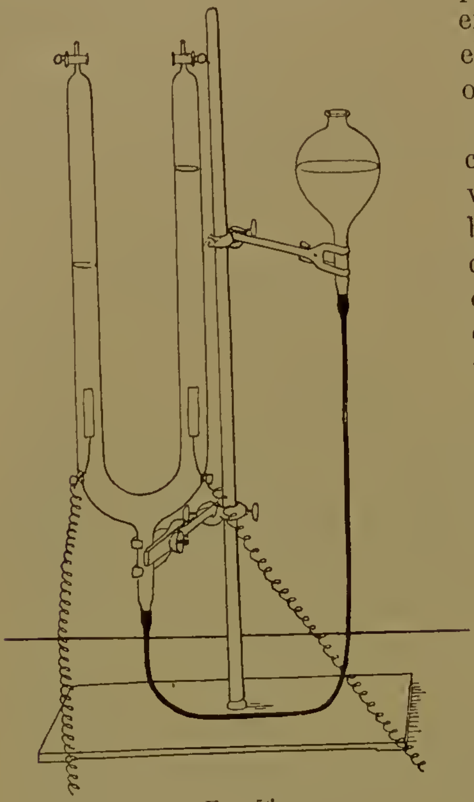
FIG. 56.

The water[1] is contained in a U-tube, the limbs of which are fairly long and closed at the top by taps. At the lower part of the tube platinum wires are sealed in, and to these are attached two plates of the same metal by means of which the electric current is conducted into the liquid. At these plates oxygen on the one side, and hydrogen on the other, are evolved, the gases ascending in the limbs and collecting underneath the taps. The displaced liquid passes through a third tube at the foot, and through a rubber tube into a collecting vessel at the side, which can be placed in any desired position. After the current has passed some time and a sufficient quantity of gas has been evolved, the following facts can be recognised:—

The evolved gases do not occupy the same volume. On the contrary one appears in larger amount, and on making a measurement it is found that its volume is twice as great as that of the other.

The smaller quantity of gas consists of oxygen which can be identified by means of a glowing splinter.

The other gas, which is formed in double the volume, can be set on fire, burns with a pale flame, and proves, on closer investigation, to be hydrogen.

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[1] For this experiment one does not use pure water, but a dilute solution of sulphuric acid or caustic soda. The reasons for this and also the more exact discussion of the electrolytic processes will be given at a later point (Chap. IX.).

The Law of Combination of Gases by Volume.—In view of the remarkably simple relation we have just met with in the case of the combination of the gases hydrogen and oxygen, the question at once arises whether we are dealing here with a more general law. After this first relation had been established by Gay-Lussac and Humboldt (1805), the former at once asked himself the more general question, and in 1808 answered it to the effect, that *all gases which undergo chemical transformation with one another, do so in the ratios of whole numbers, by volume.* If, therefore, any gases A_1, A_2, A_3, . . . interact chemically with one another, and form the gases B_1, B_2, B_3, . . . , the volumes occupied by the quantities of the interacting gases can be represented by the equation

$$m_1A_1 + m_2A_2 + m_3A_3 + \ . \ . \ . \ = n_1B_1 + n_2B_2 + n_3B_3 + \ . \ . \ .$$

where m_1, m_2, m_3, . . . and n_1, n_2, n_3 . . . are whole numbers, and, mostly, *small* whole numbers.

Gases, therefore, react with one another in simple rational proporions by volume, and the volumes of the gases produced likewise exhibit simple relations to the initial substances.

If we imagine one of the reacting gases withdrawn from the total amount, the ratio of the others will not be altered thereby. The law ve have enunciated, therefore, must also hold good when one or everal of the substances produced do not exist as gases at the temperaure of the experiment, but separate in the solid or liquid state. We an extend the theorem, therefore, to read: *If, in any chemical proesses, several gases appear or disappear at the same time, they do so always in simple ratios by volume.*

The Law of Combining Weights.—The series of conclusions which can be drawn from the law of gaseous combination by volume is ot exhausted by the laws we have just enunciated. Evidently, it is uite arbitrary to apply the law only to such substances as are gaseous t ordinary temperatures. For, since, with change of pressure and emperature, the volume of all gases changes in the same ratio, the aw of volumes remains valid for any (concordant) pressures and temeratures. Accordingly, one can imagine the temperature high enough nd the pressure low enough for all the substances to be gaseous; the w of volumes would then be valid for all chemical processes.

It appears, now, to be a superfluous piece of work to deduce conusions for a condition which cannot be experimentally produced, and e conclusion just drawn would also have no special significance were not that it can be turned to account in the case of a further conseience which can be directly put to the test.

Imagine equal volumes of a number of gaseous substances to be easured off at the same pressure and temperature. When, then, chemical reactions take place between any of these substances, the amounts which react with one another may be represented by these volumes, a whole number of such volumes of each gas being always used up, and also a whole number of such volumes of new substances being produced.

Each of these volumes, however, represents a quite definite weight of the substance in question, which is proportional to the gaseous density of the substance. From this it follows:—

For every gaseous substance a definite weight can be given, which has the property that the proportions by weight of all possible chemical compounds of these substances with one another can be represented by this definite weight, or by a rational multiple of it. This number is proportional to the density of the gaseous substance.

Since, as we have just seen, no limit can be given for gaseous substances, this conclusion must be extended to all substances. Calling the definite weight just mentioned by the name *combining weight*, we can state the theorem: *To every substance a combining weight can be assigned. All chemical reactions between substances take place in proportions by weight which can be represented by the combining weights or by rational multiples of them.*

Such an immense extension of a law which, in the first instance, has been proved only for the comparatively small number of substances occurring in the gaseous state, requires, of course, to be minutely tested. This work was undertaken, above all, by Berzelius (1810 and ff.). The result was that the law of combining weights is, as a matter of fact, universally valid. It is the fundamental law of quantitative chemistry, and the numbers thereby fixed, the combining weights, are the real units of chemical mathematics.

We shall further remark that the combining weights are *ratio numbers*, since, of course, the choice of the unit of volume according t which the gases were compared was an arbitrary one. The questio as to the unit of the combining weights, or the arbitrary number t which the others are to be referred, cannot be discussed in detail unti later. Here it is sufficient to state that the number 16 for oxyge has been adopted as reference number.

Further, we have to take the following into consideration:—W imagine, first of all, the combining weights of the elements fixed These, now, can come together to form compounds which, in turn, ca form compounds with one another and with other elements. Ever compound substance, therefore, also has a combining weight. Sinc the law of the volume ratios of gases holds also for the compounds the latter substances, the combining weight of these, on account of th law of the conservation of weight, must also be equal to the sum the combining weights of the elements, or to a rational multiple this. The values of the combining weights of the compound su stances have, of course, to be so chosen that they are never smaller tha the sum of the combining weights of the elements in order to avoid fractions of the combining weights of the latter.

Combining Weight of Hydrogen.—In order to choose a value for hydrogen, we can simply assume the combining weight to be proportional to the gaseous density, so that equal volumes of the gases lso contain the same number of combining weights. According to the ratio of densities, then (p. 88), the combining weight of hydrogen must be made equal to 1·008 if oxygen is equal to 16.

A difficulty, however, arises when the product of combination, water, is taken into account. Adopting the stand-point that the ombining weights are directly proportional to the gas densities, we btain for water, from the figures on p. 122, the value 9·008. The ombining weight of water would, therefore, not be equal to the sum f the combining weights of its elements, but only to half this.

It is, therefore, not possible to make the combining weights simply roportional to the gas densities or to the molar weights (p. 89) vithout falling into contradictions. In the course of the developnent of chemistry attempts have been made in various ways to remove hese contradictions. The following is the method now universally dopted :—

The combining weights are determined so that there is always a whole umber (no fractions) of combining weights contained in the molar weights.

If we make the *molar* weight of oxygen, as has already been one, equal to 32, and that of hydrogen to 2·016, the molar weight f water vapour must be put equal to 18·016, as can be seen from e density data on p. 122. If, on the other hand, we put the *combing* weight of oxygen equal to 16, and that of hydrogen to 1·008, we n fulfil the requirement which has just been stated. The molar eight of oxygen, and likewise of hydrogen, then contains two comning weights of the elements, while in aqueous vapour there are ntained two combining weights of hydrogen and one of oxygen, the m of which is equal to the combining weight of water. In the case this substance, therefore, molar weight and combining weight incide.

The choice just made has shown itself to be sufficient also for all her compounds in which hydrogen and oxygen are contained. Not e of these numerous substances has exhibited a molar weight in ich there occurs a smaller amount than 16 parts of oxygen or 1·008 rts of hydrogen.

The Combining Weights of the Elements.—By determining w much of each element combines with one combining weight, or 16 rts, of oxygen, the combining weight of that element is obtained.

Now, to be sure, it is not necessary to assume that only one comning weight of the other elements always combines with one nbining weight of oxygen, but, as in the case of water, there may reasons for regarding other assumptions as better. In fact, there are numerous instances where such is the case. Since these, however, follow only from a more exact knowledge of the chemical relations of the elements, the discussion of them must be postponed, and we shall immediately give the results here.

Further, the other elements are not all capable of giving compounds with oxygen, although the majority of them are. Also, the oxygen compounds of some elements cannot be exactly investigated with regard to their composition, or analysed, so that the question arises how, in these cases, the combining weights are determined.

On this point information is afforded by the definition of combining weight given on p. 140. These numbers are valid not only for the compounds with oxygen, but also for all compounds of the elements with one another. If then the fact has been established, that an element B combines with oxygen so that for every 16 gm. of oxygen there are present *b* gm. of the element, and if there be determined the amount *c* of a third element C which can unite with *b* gm. of B, then the number *c* is also the combining weight of the element C.

In general: The weight of an element which can combine with the combining weight of another element, referred to oxygen = 16, is equal to the combining weight of that element.

By means of this principle, it is evident that the combining weight of one and the same element can be determined in very different ways, and through the medium of entirely different elements. This has, in fact, been done, and the combining weights, determined by such different methods, have always proved to be identical within the limit of the experimental error. In these investigations we have an exceedingly important confirmation of the law of combining weights.

The following table gives a list of the combining weights of the elements so far as known with some degree of accuracy; the values are given such that there may be an error in the last place of less than half a unit.

Table of the Combining Weights of the Elements

1. Aluminium	Al = 27·1	17. Cobalt	Co = 59·0
2. Antimony	Sb = 120	18. Copper	Cu = 63·6
3. Argon	A = 39·9	19. Erbium	Er = 166
4. Arsenic	As = 75·0	20. Fluorine	F = 19
5. Barium	Ba = 137·4	21. Gadolinium	Gd = 156
6. Beryllium	Be = 9·1	22. Gallium	Ga = 70
7. Bismuth	Bi = 208·5	23. Germanium	Ge = 72
8. Boron	B = 11·0	24. Gold	Au = 197·2
9. Bromine	Br = 79·96	25. Helium	He = 4
10. Cadmium	Cd = 112·4	26. Hydrogen	H = 1·008
11. Cæsium	Cs = 133	27. Indium	In = 114
12. Calcium	Ca = 40	28. Iodine	I = 126·85
13. Carbon	C = 12·00	29. Iridium	Ir = 193·0
14. Cerium	Ce = 140	30. Iron	Fe = 56·0
15. Chlorine	Cl = 35·45	31. Krypton	Kr = 81·8
16. Chromium	Cr = 52·1	32. Lanthanum	La = 138

Table of the Combining Weights of the Elements—*Continued*

33. Lead	Pb = 206·9	55. Scandium	Sc = 44·1
34. Lithium	Li = 7·03	56. Selenium	Se = 79·1
35. Magnesium	Mg = 24·36	57. Silver	Ag = 107·93
36. Manganese	Mn = 55·0	58. Silicon	Si = 28·4
37. Mercury	Hg = 200·3	59. Sodium	Na = 23·05
38. Molybdenum	Mo = 96·0	60. Strontium	Sr = 87·6
39. Neodymium	Nd = 143·6	61. Sulphur	S = 32·06
40. Neon	Ne = 20	62. Tantalum	Ta = 183
41. Nickel	Ni = 58·7	63. Tellurium	Te = 127
42. Niobium	Nb = 94	64. Thallium	Tl = 204·1
43. Nitrogen	N = 14·04	65. Thorium	Th = 232·5
44. Osmium	Os = 191	66. Thulium	Tu = 171
45. Oxygen	O = 16·00	67. Tin	Sn = 118·5
46. Palladium	Pd = 106	68. Titanium	Ti = 48·1
47. Phosphorus	P = 31·0	69. Tungsten	W = 184
48. Platinum	Pt = 194·8	70. Uranium	U = 239·5
49. Potassium	K = 39·15	71. Vanadium	Vd = 51·2
50. Praseodymium	Pr = 140·5	72. Xenon	X = 128
51. Rhodium	Rh = 103·0	73. Ytterbium	Yb = 173
52. Rubidium	Rb = 85·4	74. Yttrium	Y = 89
53. Ruthenium	Ru = 101·7	75. Zinc	Zn = 65·4
54. Samarium	Sa = 150	76. Zirconium	Zr = 90·7

A glance at the table shows that the combining weights vary within very wide limits; in round numbers, from 1 to 240. Between these they are distributed pretty uniformly over the whole series of numbers.

It is also remarkable that the combining weight of hydrogen is, as can be seen from the table, so near unity, without being exactly equal to it. This has the following historical reason:—The combining weights were at first so determined that hydrogen was put equal to unity. Since, however, only very few elements are capable of forming hydrogen ompounds, the indirect method just described had to be applied for determining their combining weights. This was carried out by ascer-aining the combining weight of oxygen with reference to hydrogen = 1, and then referring the other elements, by means of their oxygen ompounds, to the number for oxygen thus determined, which had een found equal to 16·00. For such elements, in the case of which xygen compounds could not be investigated, measurements were rried out with the help of elements whose combining weights had een determined with reference to oxygen and not to hydrogen. xygen was, therefore, the practical basis of *all* the combining weights, nd hydrogen was only chosen formally as such because its combining eight was the smallest of all.

In recent times, now, the discovery was made that the ratio 1 : 16 r hydrogen : oxygen, had been rather inaccurately determined, and at it is really 1·000 : 15·88, or 1·008 : 16·00. The choice had, erefore, to be made as to which of these two relations should be tained, and the decision was given in favour of the second. The essential reason for this was that the number 16 for oxygen had, really, always formed the real basis of all determinations and calculations with the combining weights. If, therefore, the number 16 were changed to 15·88, all numbers referred to it must also be changed. By retaining, however, the number 16 for oxygen, and changing only that for hydrogen from 1 to 1·008, no such recalculation of the other numbers was required, since only the value for hydrogen was affected. For the future, then, the number 16 has been adopted as the basis of the combining weights of the other elements.

The Accuracy of the Law of Combining Weights.—Since the gas law is only a limiting law (p. 90), and since we have based the law of combining weights on it, the question must arise as to what degree of accuracy this law possesses, and whether it also is to be regarded as a limiting law.

Experience has shown that *the law of the combining weights is as exact as the law of the conservation of weight, i.e.* the limit of its accuracy has, as yet, not been found.

This is connected with the circumstance that the law of combining weights remains valid whether we are dealing with gases or with substances in any other physical state. The *deduction* of the law from the law of volumes of gases was made for the sake of clearness; its *foundation* in fact, however, is the result of quantitative chemical analysis.

Chemical Symbols and Formulæ.—Since all compound substances can be represented as combinations of the elements, their composition can be designated shortly by stating the elements from which they are produced. This designation takes a very simple form when, instead of the names of the elements themselves, abbreviated, readily intelligible symbols are employed.

Such a method has been in use almost as long as chemical writings exist, for even in the oldest alchemistic records the most important of the substances occurring are represented by individual symbols. The use of such a symbolic language also exists throughout the whole development of scientific chemistry. These very manifold attempts, however, received a permanent form only after the law of combining weights was discovered, and after Berzelius had made an exceedingly simple and suitable proposal for fixing the symbols.

Whereas, namely, all former symbols had been more or less arbitrarily chosen and offered no hold to the memory, Berzelius derived them from the names of the elements themselves, introducing the initial letter of these as symbol for the element. In order to put differences in language out of account, he used the Latin or Greek names as the basis of the abbreviations. In those frequent cases where several elements commence with the same letter, the aid of an additional characteristic letter is taken.

In this way the symbols given in the table on p. 142 were obtained.

While, in former times, such symbols had only a qualitative signification, the law of combining weights makes it possible to attach to them also a quantitative meaning. This consists in also understanding by the symbol of each element a *combining weight* of that element. The symbol O for oxygen, therefore, not only signifies that element, but also 16 parts of it by weight.

Since the combinations between the elements take place only in the proportions of the combining weights and of whole multiples of these, it is only necessary, in order to state the qualitative and quantitative composition of a compound, to write down the symbols of the elements present and the factors by which the combining weights of each have to be multiplied. For the sake of convenience it has become customary to write the factors in the position of suffixes to the symbol of the element. The composition of water of two combining weights of hydrogen and one of oxygen is, therefore, written in the form H_2O, the factor 1 being, as is usual, omitted.

This formula expresses the fact that water is produced from 2 × 1·008 parts of hydrogen and 1 × 16·00 parts of oxygen by weight, and that it contains these and no other elements.

In the case of substances whose gaseous density and molar weight can be determined, it is further usual to write the formulæ so that they express a molar weight of the substance designated. Since the combining weights were chosen on the principle that a whole number of combining weights is contained in a molar weight, this can always be done without having to use fractions of a combining weight. Such formulæ, therefore, allow also of deducing the gaseous density, to which, of course, the molar weight is equal.

Chemical Equations.—By reason of the laws of the conservation of weight and the conservation of kind (p. 60), chemical processes can be written in the form of equations in which the substances are represented by their symbols. As a result of the two laws named, we have, irst, that the *weights* on both sides of a chemical equation must agree; and, second, that on each side of the equation *the same elements with the ame number of combining weights must occur.* The way, however, in which the elements are combined with one another can be different.

For example, the formation of water from oxygen gas and hydrogen gas is expressed by the following equation:—

$$O + 2H = H_2O.$$

It is usual to write the equations in such a manner that the itial substances stand on the left hand, and those formed in the action, on the right. Since at a very high temperature water ecomposes into its elements, this process would be written in the everse order:—

$$H_2O = O + 2H.$$

As can be seen, when more than one combining weight of the substances under consideration take part in the reaction, the corresponding factors are written *before* the formula, whereas the factors of the elements which are present in more than one combining weight *in a compound* (such as hydrogen in water) are written as a suffix (p. 145).

If, as is very frequently the case, it is desired to express, at the same time, by means of the formula, the molar weight of the substances designated, the equation has, generally, to be written otherwise. A molar weight of hydrogen and of oxygen each contains two combining weights of the elements; we must, accordingly, write

$$2H_2 + O_2 = 2H_2O.$$

From such an equation we can, at the same time, from the meaning of a molar weight, tell the volume ratios of the reacting gases. The present example shows directly that one volume of oxygen and two volumes of hydrogen yield two volumes of water vapour.

The formulæ which signify molar weights are not as yet distinguished from those intended only to denote combining weights. This must be called an imperfection. In this book molar weights, where such are known, will generally be written.

The Atomic Hypothesis.—For the representation of the simple and comprehensive laws to which the weight and volume ratios of chemical compounds are subject, a hypothetical conception has been in use since the time these laws were first discovered, which affords a very convenient picture of the actual relations, and possesses, therefore, a great value for the purposes of instruction and investigation. For this reason the above hypothesis has been made the basis of the language and modes of representation throughout the whole of chemistry, so that the results of chemical investigation are almost exclusively communicated in that language. For this reason alone a knowledge of the hypothesis is necessary.

* In general, an hypothesis is an *aid to representation.* Of the phenomena of the outer world, some are so familiar to us from repeated experience, that we know the relations which exist among them with great certainty. If now we find a new and unfamiliar class of phenomena, we unconsciously seek for similar ones among those that are known. If we succeed in discovering such a similarity we gain two advantages. In the first place, the fixing of the new facts in the memory is very greatly facilitated by the use of the similarity, and in the second place, the similarity affords us a means of making probable guesses concerning the behaviour of the new phenomena under conditions under which they have not yet been investigated.

* As compared with the less known, the basis of the hypothesis forms such a group of similar and well-known phenomena. Since of all phenomena those of mechanics are usually the most familiar to us, by far the most hypotheses are mechanical analogies of non-mechanical phenomena.

* The same character is possessed also by the present hypothesis. The peculiarities of the weight relations of chemical processes are "explained" by a definite assumption concerning the mechanical nature of the substances.

This assumption consists in regarding all substances as composed of very small particles or *atoms*. The atoms of each elementary substance are alike among themselves, and single, and are different from the atoms of every other element. The atoms of a chemical compound are alike among themselves, but are composed of the atoms of the elements by the interaction of which they are produced.

From these assumptions the laws of chemical combination follow directly. The assumed identity of the atoms or the atomic groups which form a definite substance gives a picture of the theorem of the definiteness of the properties of every substance. The assumption of the difference of the nature of the atoms of the different elements explains the inconvertibility of the elements into one another, and the assumption that the atoms of the elements remain intact in the compounds, and are only differently grouped together to form, in each case, an atom of the compound, makes the law of the connection between the derivatives of each element clear.

On the same foundation also, the quantitative laws of combination re made intelligible. Since all the atoms of a definite element are ssumed to be identical among themselves, we must also assume dentity for the weight of each atom. When, therefore, two or more lifferent atoms combine in a definite manner to form a compound, the roportions by weight in which the compound is formed are also fixed y the number and kind of the elementary atoms. Since, finally, all ompounds are regarded as congeries of the corresponding elementary toms, the proportions by weight of these must be represented univer- ally by the numbers which are obtained by multiplying the weight of ach kind of atom by the number of them. In this picture, therefore, he combining weight of an element assumes the signification of the eight of an atom, and the designation *atomic weight* in place of com- ining weight has a universal currency.

* Within the limits here given, the atomic hypothesis has proved be an exceedingly useful aid to instruction and investigation, since greatly facilitates the interpretation and the use of the general laws. ne must not, however, be led astray by this agreement between cture and reality, and confound the two. So far as we have treated em, the chemical processes occurred in such a way as if the bstances were composed of atoms in the sense explained. At best

there follows from this the *possibility* that they are in reality so; not, however, the *certainty*. For it is impossible to prove that the laws of chemical combination cannot be deduced with the same completeness by means of quite a different assumption.

* One does not require, therefore, to give up the advantage of the atomic hypothesis if one bears in mind that it is an illustration of the actual relations in the form of a suitable and easily manipulated picture, but which may, on no account, be substituted for the actual relations. One must always be prepared for the fact that sooner or later the reality will be different from that which the picture leads one to expect.

* Especially, when any other well-founded speculation leads to a variance with the atomic hypothesis, one must not, on that account, regard the speculation as wrong. The blame can quite well attach to the hypothesis.

The atomic hypothesis, in the sense developed here, was put forward by J. Dalton in the year 1805; the testing of its most important consequence, the law of combining weights, was performed by Berzelius (p. 140). On account of its entire agreement with experiment, the atomic hypothesis attained to a position of great consideration and universal application, so that, even at the present day, it rules almost exclusively in chemistry.

In this book also we shall not deviate essentially from the general usage. Still, it would certainly be to the interest of the science if greater care were exercised in this connection, and for that reason we have here laid stress on using the forms of expression of the atomic hypothesis as sparingly as ever the present usage of language will permit.

The Molecular Hypothesis.—Just as the laws of weight in chemical processes, so also the laws of volume in the interaction of gaseous substances have given rise to mechanical hypotheses, which have played a similar though not so important a part in the development of chemistry as the atomic hypothesis.

Since gases combine in equal or in multiple volumes, the most natural assumption is that the same number of atoms is contained in equal volumes of the different elementary gases. In fact, this assumption was at first made.

With this assumption, however, the fact that two volumes of hydrogen and one volume of oxygen yield two volumes of aqueous vapour cannot be brought into agreement. For, let the number of atoms in the unit of volume be N, and let us make the appropriate assumption that the same law holds also for the aqueous vapour. 2N atoms of water must be produced from N atoms of oxygen and 2N atoms of hydrogen, *i.e.* in each atom of water half an atom of oxygen must be contained.

This is not the only difficulty of this kind; on the contrary, similar ones are encountered in nearly every case of combination between gaseous substances.

To avoid this contradiction, therefore, it was necessary to distinguish between the atoms and the smallest particles of the gases. If we assume that the latter, which are called *molecules*, are composed of several atoms, the volume ratios of the gases can be satisfactorily represented.

The consideration of all known cases has shown that a very simple assumption suffices here. The contradiction can be avoided if, in the case of the elementary gases, *e.g.* oxygen and hydrogen, the molecules are regarded as being formed each of *two* atoms. In the case of other elements other assumptions are in part necessary, and these will be discussed when we come to them.

According to this assumption there are contained in equal volumes of the different gases, not an equal number of atoms, but an equal number of molecules. If, as mentioned, the molecules of oxygen and hydrogen each consist of two atoms, and if N is the number of molecules (not of atoms) in the unit of volume, we have the following calculation :—

One volume of oxygen contains N molecules, and therefore 2N atoms. With two volumes of hydrogen (=4N atoms) it forms two volumes of aqueous vapour, in which, therefore, 2N molecules of water must be contained. If one assumes that each water molecule consists of one atom of oxygen and two atoms of hydrogen, exactly 2N molecules of water vapour can be formed from the atoms present, and the actual relations receive a correct representation.

The molecular hypothesis stands to the conception of the molar weight (pp. 89 and 141), previously introduced on the basis of the law of Gay-Lussac, in the same relation as the atomic hypothesis stands to the conception of the combining weight, and the molar weight appears, in the light of the hypothesis, as the relative weight of a molecule, or the *molecular weight*. For, if an equal number of molecules is assumed in equal volumes of the different gases, the weights of the different molecules must be to one another as the weights of equal gas volumes, *i.e.* as the gaseous densities or the molar weights.

The requirement that the molar weights shall be expressible in integral values of the combining weights assumes the clearly intelligible form, that no fractions of atoms are to be assumed in the molecules.

The name molecular weight is in general use for the previously deduced conception of the molar weight. It may also be employed independently of the hypothesis on which it is based, if one bears in mind that it expresses an actual relation, viz. the gaseous density.

* The hypothesis just developed was put forward by Avogadro and Ampère almost simultaneously in the years 1811 and 1812. The assumption that in equal volumes of gases equal numbers of

molecules are contained is sometimes called the law of Avogadro. This is misleading, since a hypothesis can never be a law. It may be called the *postulate* of Avogadro. The *law* on which these considerations are based is that of the rational volume ratios in the reactions between gases, discovered by Gay-Lussac.

The Action of Sodium on Water.—Of the changes which take place by the interaction between water and sodium (p. 83), we have, as yet, considered only the evolution of hydrogen from the water. We shall now pass to the investigation of the other products.

In the first place, the water which had been used for the reaction is, in its outward appearance, unchanged; the product which has been formed from the sodium must therefore be soluble and yield a colourless solution. That something new is present, is shown, however, by the taste, which is unpleasantly soap-like, and by its power of exhibiting actions not shown by water. One of the most conspicuous of these actions is the alteration of certain colouring substances. A piece of paper coloured purple with litmus (a colouring substance extracted from lichens) immediately becomes blue when moistened with the liquid formed. A piece of colourless paper containing the artificial dye, *phenolphthalein*, which is used by electricians as "pole reagent paper" for determining the direction of the electrical current in a conductor, becomes coloured purple-red, and paper coloured with the yellow vegetable dye *turmeric*, becomes red-brown.

What takes place in the case of these changes cannot be explained till later; they serve, in the first place, as an identification sign for the substance produced.

To obtain this substance in the pure condition, the water in which it is dissolved must be removed. This is done by heating the solution till it boils; the water then passes into the form of vapour and escapes, while the dissolved substance, which is not volatile, remains behind.

This method which is generally used for obtaining the substances present in solutions when they are not or are only slightly volatile, is called *evaporation*. The apparatus used for the purpose vary according to the scale on which the operation is carried out; they all agree, however, in being of such a shape that the surface of the evaporating liquid is kept as large as possible. For the velocity of evaporation, or the amount of liquid evaporating in unit time, increases, *ceteris paribus*, proportionally with the evaporating surface.

Caustic Soda.—On evaporating the solution produced by the action of sodium on water, a white substance is obtained which is solid at ordinary temperatures, but which readily fuses and redissolves in a small quantity of water with development of heat. It is the same substance as served in the combustion experiment described on p. 35 for retaining the gaseous and vaporous products of combustion. If a little of the substance be dissolved in water the liquid exhibits all the colour reactions of the solution produced by the action of sodium on water.

That this substance also contains oxygen as well as sodium follows from the fact that it was formed, with evolution of hydrogen, from water and sodium ; in it there must be present the oxygen which was previously in combination with the hydrogen evolved. The product, however, need not consist of sodium and oxygen *only;* it may also contain hydrogen from the water.

That it does, in reality, still contain hydrogen is shown by the following experiment. If a little of the substance is mixed with finely powdered iron, and the mixture heated in a small tube of resistant glass, closed by a cork through which a drawn-out glass tube passes (Fig. 57), there soon escapes from the opening a gas which can be set on fire, and can be immediately identified as hydrogen by the film of moisture formed on a cold glass held over it.[1] Since the iron, being an "element," contains no hydrogen this must come from our substance.

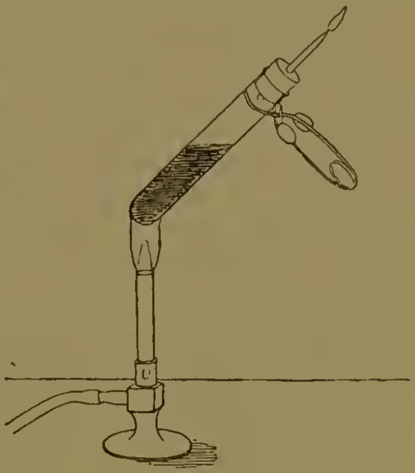

FIG. 57.

The result of more exact analysis shows that the product consists of sodium, hydrogen, and oxygen in the proportions 23·05 : 1·01 : 16·00 by weight. It contains, therefore, an equal number of combining weights of hydrogen and oxygen. The combining weight of sodium has been found equal to 23·05 ; since the chemical symbol for sodium is Na, the formula NaOH is obtained for the compound. In chemical language it is called *sodium hydroxide,* or *caustic soda.*

The name sodium hydroxide is intended to indicate that, besides oxygen, hydrogen is also contained in the compound.

Compounds which are constituted in the same way as sodium hydroxide, *i.e.* which, along with the metal, contain an equal number of combining weights of oxygen and hydrogen, occur in large numbers, for almost every metal can form such compounds. In consequence of their containing these elements in common they possess certain concordant properties, so that it has been found convenient to give them a special family name, and also to give a special designation to the group OH. The metallic compounds are called *bases,* and the group OH, *hydroxyl.* Bases are, therefore, compounds of metals with hydroxyl.

Not all the metals combine with hydroxyl in such a way that to one combining weight of the metal also *one* hydroxyl is present. On the contrary, other reasons have often led to assuming combining weights for the metals such that two, three, and even four hydroxyl groups are united with one combining weight of the metal. The corresponding hydroxides or bases then have the formulæ $M(OH)_2$, $M(OH)_3$, $M(OH)_4$, where M is the symbol of the metal. These metals, and also the bases produced from them, are accordingly called di-, tri-, and tetravalent.

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[1] The flame of the hydrogen is generally coloured yellow, and this from the same cause as given on p. 84.

The bases, in so far as they are soluble in water, all behave in the same way as caustic soda with respect to the colouring substances. These reactions, then, belong, not to the different metals from which the bases have been produced, but to the common component, hydroxyl.

Deliquescent Substances.—On evaporating solutions of caustic soda it is found that the last portions of water are difficult to remove, since the vapour pressure of the concentrated solutions is very much smaller than that of pure water.

Conversely, caustic soda, freed from water, has the property of becoming moist in air by condensing on itself the aqueous vapour present in the latter (p. 122), and it ultimately takes up so much water that it liquefies to a solution. Caustic soda, therefore, is called a *deliquescent* substance.

The property of deliquescing is not one belonging exclusively to caustic soda, but also belongs to many easily soluble salts. The condition for it is that a solution is produced which has a smaller vapour pressure than the mean vapour pressure of the water in the air. Such a substance continues to withdraw water from the moist air until the vapour pressure of the latter becomes equal to that of the solution produced. If the air is renewed, as in the case of substances placed in open vessels, the process comes to an end only when a solution has been produced, the vapour pressure of which is equal to that of the air.

Since, on an average, the air is saturated with aqueous vapour to an extent of 60 to 70 per cent, all substances will deliquesce which can form solutions the vapour pressure of which is less than 0·6 of that of water at the same temperature.

CHAPTER VIII

HYDROGEN PEROXIDE

Hydrogen Peroxide.—By means of reactions, the details of which cannot be understood till later (Chap. XXV.), it is possible to prepare a second compound of hydrogen and oxygen which has a different composition and essentially different properties from water. This compound is called *hydrogen peroxide*, a name which expresses that it contains more oxygen than water, which would have to be called hydrogen oxide.

The composition of hydrogen peroxide is given by the formula H_2O_2. This states that for the same amount of hydrogen double as much oxygen is contained in the new compound as in water. In numbers the formula shows that the compound is composed of 2 × 1·008 parts of hydrogen and 2 × 16·00 parts of oxygen, by weight; its molar or molecular weight, therefore, amounts to 34·016. If the weights of oxygen and hydrogen present are divided by this number and multiplied by 100, the percentage composition of hydrogen peroxide is obtained. The result is 94·1 per cent oxygen and 5·9 per cent hydrogen.

Hydrogen peroxide is a thickish liquid with a density 1·5, and is colourless. It is very difficult to prepare quite pure, and when it is obtained it very readily decomposes spontaneously, so that its existence is always only quite a passing one. The decomposition takes place according to the equation

$$2H_2O_2 = 2H_2O + O_2,$$

.e. the substance decomposes into water and oxygen gas.

On account of its great readiness to decompose, hydrogen peroxide s usually prepared and used in the form of a dilute solution, in which t is much more stable. Since it dissolves in all proportions in vater solutions of any desired strength can be prepared, and the trength is usually stated by the number of volumes of oxygen vhich can be evolved from one volume of the solution on decomposition. Since 2 × 34 gm. of peroxide evolve 32 gm. of oxygen, which under ordinary conditions occupy a volume of 22·4 lit. (p. 89), it follows that every gram of peroxide evolves 353 cc. of oxygen. A one per cent solution, containing, therefore, 1 gm. in 100 cc., accordingly evolves 3·53 times its volume of oxygen, and the solution ordinarily used of strength 10 volumes of oxygen contains, therefore, rather less than 3 per cent of peroxide.

This solution looks like water, but has a peculiar astringent taste. It has no definite smell. It slowly evolves oxygen so that it must not be kept in perfectly close vessels, since these could thus be readily burst. The decomposition is much less in the cold than in the heat, and is, moreover, very greatly influenced by the presence of other substances. The peroxide can be best preserved in a solution containing a small quantity of some acid or a little spirit of wine.

Hydrogen Peroxide as Oxidising Agent.—The ease with which the peroxide decomposes into water and oxygen is also seen in the presence of such substances as can chemically combine with oxygen. Hydrogen peroxide is therefore an *oxidising agent*. Since gaseous oxygen is spontaneously formed from the peroxide, and the reverse reaction does not take place to a measurable extent, we must conclude that the peroxide is a stronger oxidising agent than gaseous oxygen, *i.e.* the peroxide can still give up oxygen to such substances as are not capable of forming compounds with oxygen *gas*. This conclusion is based on the following reasons:—

It can be proved generally that the action of any oxidising agent can, theoretically, be replaced by the action of oxygen gas under an appropriate pressure. The highest pressure of oxygen corresponds to the strongest oxidising agent, and *vice versa*. Imagine this pressure determined for each oxidising agent (which is generally possible by indirect means), we can then arrange these in a series of decreasing pressures, and we can assert that with a higher oxidising agent we can, indeed, prepare every lower one from oxygen and the other component, but not conversely, just as the pressure of oxygen can spontaneously, only diminish, but not increase. Since oxygen gas can be prepared from hydrogen peroxide, but not hydrogen peroxide from oxygen, the peroxide must be the higher oxidising agent.[1]

The Molar Weight of Hydrogen Peroxide.—The formula o hydrogen peroxide has been written H_2O_2, although it might hav been more simply written HO. On account of the ready decom posability of the pure peroxide, its vapour density has not as ye been measured. The question therefore arises, What is the reason for so writing the formula?

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[1] In applying this reasoning, it is necessary to know that in the case of a oxidising agent existing in the condition of a solution, its position in the series i dependent on the concentration of the solution, and is all the lower the more dilut the solution is made. The same part is played by the pressure of gases, as, indee follows from what has been said. For solid substances and unmixed liquids, howeve the position in the series is fixed, and undergoes an appreciable alteration only throug change of temperature, which varies from case to case.

The answer is that the molar weight of substances can be determined not only from their gaseous density, but also from their behaviour in solution. It has been mentioned on p. 133 that all substances in solution lower the freezing point of water (and also of every other solvent) proportionally to the concentration, and that a similar law holds for the lowering of the vapour pressure (or the elevation of the boiling point).

One is now led to ask the question, What quantities of the different substances are required to produce the same lowering of the freezing point? The answer which experiment has given to this question is very remarkable. *The quantities of substances which produce the same lowering of the freezing point are in the ratio of the molar weights.*

If the former reasoning (p. 134) be applied to the case of the lowering of the vapour pressure, we must make the further statement, that the amounts of *substances which produce an equal lowering of the vapour pressure also stand to one another in the ratio of the molar weights.*

The elevation of the boiling point is proportional to the lowering of the vapour pressure. We can therefore enunciate the further theorem, that *those quantities of different substances which raise the boiling point of the solvent by the same amount stand to one another in the ratio of the molar weights.*

These laws are of especial importance, because of the fact that they allow of the determination of the molar or molecular weight in the case of those substances also which cannot be investigated in the condition of vapour, either because of the fact that at the temperatures attainable their vapour pressure does not have a measurable value, or because, on attempting to vaporise them, they decompose. By experiments on substances whose molar weight had been determined by measurements of the vapour density, it has been possible to satisfy oneself of the universality of the laws just stated, so that these can be applied with certainty in those cases also where this control is not possible.

From the theoretical side also these laws are assured, and the general conditions of their validity have been determined. Into these questions, however, we shall not yet enter, since the empirical knowledge is sufficient, in the first place, for their application.

* In order to apply one of these methods, *e.g.* the depression of the freezing point, to the determination of the molar weight of a new substance, one first determines the depression which is produced by the solution of a substance whose molar weight is known. If the amount of the new substance required to produce the same depression be then determined, the weights of the two substances are in the ratio of their molar weights, and the molar weight of the new substance is found by a simple calculation in proportion.

* Thus it has been established that when one gram-molecule or one *mole* (the molar or molecular weight of a substance expressed in grams) of any substance is dissolved in a litre or 1000 gm. of water, the solution produced freezes at – 1·850°. If we dissolve g grams of the new substance in G grams of water, and if we observe for the solution a depression d of the freezing point, we can perform the following calculation :—The amount of the new substance dissolved in 1000 gm. of water is 1000 g/G ; this has produced the lowering d. According to the law of the proportionality between the amount dissolved and the depression, the depression 1·850° will be obtained when the dissolved amount is changed in the ratio d : 1·850. This amount, however, is equal to a mole of the substance, since the depression 1·850° is produced by one mole in a litre. Hence, if we denote a mole or the molar weight in grams by M, we have the proportion

$$M : \frac{1000g}{G} = 1{\cdot}850 : d.$$

From which there follows

$$M = 1850\frac{g}{dG}.$$

* If, then, in this equation we substitute the weights g and G of the substance and water used, and the observed depression d of the freezing point, we can calculate the molar weight M of the dissolved substance.

* The equation which is obtained for the elevation of the boiling point by dissolved substances is quite similar. The reasoning is almost word for word the same, so that it does not require to be repeated ; only the constant has a different value, viz. 520. In other words, the molar weight of the dissolved substance is obtained from the formula

$$M = 520\frac{g}{sG},$$

when the boiling-point of the solution is $s°$ higher than that of water.

* The laws which have just been deduced hold, in this simple form, only for dilute solutions. Their validity, however, does not depend on water being used as solvent, but they are valid for every solvent provided this is a pure substance. Characteristic values of the constant belong to each solvent.

Preparation of Pure Hydrogen Peroxide.—Hydrogen peroxide is much less volatile than water. When, therefore, a solution of the substance is evaporated the water passes off, and a solution, richer in peroxide, remains behind. Although the decomposability of the peroxide rapidly increases with increasing concentration, fairly strong solutions can still be obtained if one starts with very pure material, and carries out the evaporation at a moderate temperature.

Under reduced pressure the concentrated solution can finally be separated into water and almost pure peroxide. For this purpose the parts of a distilling apparatus (p. 108) are connected air-tight together, and after the liquid to be distilled has been introduced the apparatus is exhausted.

The purpose of distillation under reduced pressure is to enable one to accomplish the distillation at a *lower temperature.* Since the vapour pressure of all substances rises with the temperature, and boiling occurs when the vapour pressure has become equal to the external pressure, the substance will boil at a temperature which is all the lower the smaller the external pressure is made.

The lower the temperature, however, the less is, in general, the amount of decomposition, since the velocity of this, like that of all chemical processes, rapidly increases with rising temperature. Distillation under reduced pressure, therefore, is employed in all cases where a substance has to be distilled which is not stable at the temperature of its ordinary boiling point.

When a solution rich in peroxide is treated in this manner, whereby the temperature must be kept under 80°, water with a little peroxide first distils over and then almost pure peroxide. This distillate is collected in a separate vessel, and in this way the substance is obtained in a very pure condition. Such a process, depending on the differences of the vapour pressures, is called *fractional distillation.* In chemical practice this method finds very widespread application.

Occurrence.—Hydrogen peroxide occurs in very small quantities in nature, traces of this substance being contained in rain and snow. Likewise, small quantities of peroxide are produced in many cases of combustion and also in other oxidation processes. There are a number of very delicate reactions used for the detection of such small amounts. These, however, cannot be discussed here, since they presuppose a knowledge of other substances. They will be discussed at a suitable opportunity later (Chaps. XXIX. and XLI.).

Catalysis.—Since hydrogen peroxide can decompose spontaneously into water and oxygen, a question arises similar to that asked on p. 64 with regard to the combustion of substances in the oxygen of the air: Why, then, does the hydrogen peroxide not decompose? The answer is similar: It does decompose, but with very varying velocity. To illustrate the existing relations by an analogy, one can imagine the hydrogen peroxide replaced by liquid oxygen contained in a vessel which is not completely closed. The oxygen in this vessel is also not in a permanent condition of equilibrium, but it escapes; still, although it is in communication with a space of lower pressure, its pressure does not fall to the lower value instantaneously, but only slowly, and this with a velocity which depends on the size of the opening and on the amount of friction which takes place in the opening. If the opening is very small, it may be a long time before the escape of the oxygen becomes noticeable. Every circumstance which makes the opening more accessible will hasten the lowering of the pressure; every circumstance which makes it less accessible will lengthen the period of the existing condition.

In the case of hydrogen peroxide, now, there are, as a matter of fact, very various circumstances known which act in the sense of an enlarging or diminishing of the opening, *i.e.* which change the velocity with which this spontaneous and continual decomposition takes place. Thus, porous and powdered substances greatly accelerate the evolution of oxygen. The action is, however, by no means a purely mechanical one, for different powders of similar fineness have a very different action according to their chemical nature. Pyrolusite, which in like manner also accelerates the perfectly similar decomposition of potassium chlorate when heated (p. 62), is especially effective. By shaking a solution of hydrogen peroxide with pyrolusite in an apparatus which allows of the evolved oxygen being collected and measured, the amount of hydrogen peroxide in the solution can be easily and quickly determined.

On investigating the pyrolusite after the experiment it is found to be unchanged. Finely divided platinum, which likewise remains unchanged, acts in a similar manner. Other finely divided metals, such as copper and cadmium, do not appreciably hasten the decomposition.

Such substances which act as pyrolusite and platinum do here, so as to alter the velocity of a chemical process without themselves being changed by the process, have already been mentioned (p. 104); they are called catalysers, and the action itself is called catalytic action.

* Of the catalytic actions it can be stated generally, that *they cannot bring about reactions which would not of themselves take place spontaneously if even only with a very small velocity.* If it were the case that a reaction could be brought about by a catalyser in a direction opposite to that which it takes by the action of the participating substances alone, one could allow the substances to interact alternately with and without a catalyser, and thereby, time after time, obtain reversed processes. These processes could be used to perform work, and one could thus establish a *perpetuum mobile* of the second kind (p. 133), which is in opposition to experience. Thus it is not to be expected that a catalyser could be found through the action of which oxygen and water could be caused to combine to form hydrogen peroxide.[1] For the discovery of such a substance would be identical with the

experimental refutation of the law of the impossibility of a *perpetuum mobile* of the second kind.

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[1] This holds good for pure peroxide or fairly concentrated solutions. In the case of very dilute solutions other relations obtain, and the spontaneous formation of small traces of peroxide becomes possible.

Explosive Properties of the Peroxide.—Approximately pure hydrogen peroxide is a dangerous substance, since it readily undergoes a sudden decomposition with explosion. The cause of this is that in the decomposition of the peroxide into water and oxygen heat is developed. If the decomposition has begun at one point the surrounding portions become warmed, the decomposition is accelerated, fresh amounts of heat are developed, and in this way the processes mutually advance one another to the point of rapid reaction which is called explosion.

This behaviour is exceptional, since most reactions take place in such a way that they check themselves (p. 130). For example, when water evaporates, the residue becomes colder and the vapour pressure diminishes. That hydrogen peroxide behaves in the reverse manner is due to the fact that it does not at all represent a state of equilibrium of the participating elements, but a temporary state which can be observed during a certain time, only because the approach to the state of equilibrium takes place with a certain degree of slowness.

Even in the case of dilute solutions of the peroxide the heat development during decomposition, under the influence of pyrolusite or platinum, can be easily detected by means of a thermometer, for the temperature rises quite considerably. The ordinary solution, which evolves a tenfold volume of oxygen, would, on sudden decomposition, rise in temperature by about 20° if loss of heat were avoided.

Heat Effects.—To obtain a knowledge of those heat effects which accompany chemical processes is an important task for science, since it is of account for very many general questions. The significance of these phenomena is that the amounts of heat given out and taken in are a measure of the *changes of energy* connected with the chemical processes. Since, now, the chemical processes are the source of the energy which all living things, plants as well as animals, require for the maintenance of life ; since, also, the energy used in the manufactures is derived mainly from chemical sources, the importance of such measurements is readily seen. We shall here shortly explain the principles of such investigations.

It has already been mentioned that heat is a kind of energy. It s distinguished by the property that it is produced with especial ease rom the other forms of energy. When any chemical reaction occurs he substances which are produced have, in general, a different energy rom the original ones, and the difference of the two amounts appears s *heat*, if, as is not difficult, the production of other forms of energy e avoided. Heat is developed if the energy of the products is smaller han that of the initial substances ; the temperature of the reacting ystem then rises. Conversely, if the substances are converted into uch as contain more energy than the original ones, the energy necessary for this is taken in the form of heat from the reacting system, and the temperature of this falls. Both cases are possible, but the former is by far the more frequent.

If the system in which the chemical reaction takes place is surrounded by a large bulk of water, the heat which is generated passes chiefly into this, or, in the converse case, is taken from it. If the weight of the water is known, and if the change of temperature be measured, then the product of the two numbers gives the quantity of heat in calories. For the unit of heat, or the calorie, has been defined (p. 117) as the quantity of heat which is necessary to change the temperature of 1 gm. of water 1°. If N gm. of water experience a change of temperature of t°, the corresponding quantity of heat is Nt calories, equal to 4·18 Nt joules.

As is evident, however, the quantity of heat developed varies with the amount of the substances, and is, indeed, proportional to this. In order to obtain definite numbers, therefore, the quantity of heat must be referred to definite amounts of substance. For this purpose the following method of procedure is in general use:—

The reaction is expressed by a chemical equation, and is imagined as taking place between as many grams of the different reacting substances as the numbers of the corresponding combining weights amount to. A quantity of any substance whose weight in grams is equal to the sum of the combining weights contained in the formula, is called a *mole* of the substance (p. 156). In short, therefore, the quantities of heat in chemical reactions are calculated for moles of the reacting substances.

The Heat of Formation of Water.—To give an example of what has just been said, let us consider the development of heat which occurs in the combination of oxygen and hydrogen. Evidently this is very considerable, since it gives rise to such a great elevation of the temperature as the experiments mentioned on p. 102 show.

The experiments which have been performed in this connection show that in this process 68,400 calories are developed, when one mole = 18·02 gm. of water is formed from its elements. An idea of this quantity is obtained on considering that, according to this, more than a litre of water could be heated from 0° to boiling through the combustion of 3 gm. of hydrogen.

* This number can be at once used for an interesting calculation. If we imagine the heat which is developed used only for raising the temperature of the aqueous vapour produced by the combustion of the detonating gas, the temperature of the flame of the oxy-hydrogen blowpipe is obtained by dividing the quantity of heat, 68,400 cal, by the amount of heat required to raise 18·02 gm. of aqueous vapour one degree, or the *thermal capacity* of this amount of vapour. Since, in round numbers, 9 calories are required to heat 18 gm. of water vapour 1°, the result of the calculation is that the temperature of the oxy

hydrogen flame must be $68,400/9 = 7600°$. This number proves, however, to be much too high, since measurements have given values which do not much exceed 2500°.

The cause of this disparity must be sought for in two directions. In the first place, the thermal capacity of aqueous vapour has the given value only at lower temperatures; at higher temperatures it becomes greater, and the temperature must therefore become lower. But then—and this is the chief point—the combination of oxygen and hydrogen to water is not at all complete at higher temperatures, but the higher the temperature is, the greater is the portion which remains uncombined. The combustion, therefore, raises the temperature of the flame only to the point where a further elevation would effect a separation of the water produced into its elements. Further, combustion then takes place only in proportion as heat is lost by conduction and radiation and must be replaced by fresh combustion. This temperature is then the true temperature of the flame; for the oxyhydrogen flame this is, as already mentioned, about 2500°.

On the basis of the law of the conservation of energy, we can state, n the first place, that the same quantity of heat, 68,400 cal., as was developed in the formation of one mole of water from its elements, will be again absorbed in the decomposition of water into ts elements. For if this were not the case, it would be possible, by he alternate formation and decomposition of a given amount of water, o cause the production or the disappearance of any desired amount f energy.

The further conclusion can also be drawn, that the same quantity f heat pro mole will always be developed, no matter in what way water is formed from its elements, whether by combustion with flame r by any other process. The correctness of this assertion can lso be proved from the law of the conservation of energy. In this ase we must only hold to the supposition that no other forms of nergy appear or disappear.

On the other hand, the development of heat must be different, if water is produced not from the gaseous elements but from some other ubstances which can yield oxygen and hydrogen. And, indeed, the ifference must amount to exactly as much as the amount of heat eveloped or absorbed in the conversion of the gaseous elements into ie compounds in question. This theorem, also, is based on the law f the conservation of energy.

With reference to the problem before us, the principle of the conrvation of energy in its most general application assumes the llowing form:—

There can, in general, be ascribed to every substance existing in definite state a definite content of energy, which is proportional to ie amount of substance, and which for a mole has a definite value. he amount of this energy is unknown to us, since we cannot in any way abstract from a substance all the energy which it contains. We can, however, measure the *differences* of energy between two substances before and after the chemical process, for these are the amounts of energy which are developed or absorbed as heat in the reaction. The energy relations of substances can be represented in the form of equations in which the energies of the single substances are so represented that their differences have definite values.

Thermochemical Equations.—From this there follows a method of stating the results of such measurements in a manner suitable for calculation. The chemical formula of a substance receives the additional significance that it represents not only the composition but also the energy content of the substance. The equation of a chemical process, then, which, apart from this, contains on either side the same elements in equal amounts (p. 145), must be supplemented by the statement of the amount of energy which is necessary to make the values of the energy on both sides also equal. This is the difference of the amounts of energy of the substances before and after the reaction, *i.e.* the amount of heat developed in the reaction.

For example, to express the change of energy in the formation of water from its elements, in the form of such an equation, we write

$$2H_2 + O_2 = 2H_2O + 2 \times 68,400 \text{ cal.},$$

which we read thus: The energy of two moles hydrogen and one mole oxygen exceeds that of two moles of water by 2 × 68,400 cal.; or: When oxygen and hydrogen unite to form water, water is produced and also an amount of energy equal to 68,400 cal. pro mole of water.

This method of writing allows, in the first place, of the results of measurement being represented in an unambiguous manner. It has the further great advantage that it also makes it possible to calculate the heats of reaction of processes which cannot be directly measured. The method of doing this will be given immediately when we come to study an actual case.

As regards the form of these calculations, it has to be further mentioned that in future the absolute unit of energy, the erg (p. 23) will be used in place of the arbitrary unit of heat, the calorie. Sinc this unit is too small for the accuracy of thermochemical measurement hitherto attained, the kilojoule, $kj = 10^{10}$ erg, is used in its place To reduce calories to kilojoules, we have the equation 1 cal. = 0·004183 *kj*, or 1 kj = 239·1 cal. The equation, therefore, for th formation of water from its elements reads

$$2H_2 + O_2 = 2H_2O + 2 \times 286 \; kj.$$

Heat Effects in the Decomposition of Hydrogen Peroxide —The development of heat which accompanies the decomposition hydrogen peroxide into water and oxygen gas (p. 159) can be repr sented in a similar manner. The result obtained by measurements is that an amount of heat is developed equal to 97 *kj* pro mole of hydrogen peroxide. We must therefore write

$$2H_2O_2 = 2H_2O + O_2 + 2 \times 97\ kj.$$

From this there follows, by rearrangement,

$$2H_2O + O_2 = 2H_2O_2 - 2 \times 97\ kj.$$

This equation differs strikingly from the former one. Whereas in the previous case the formation of the compound was accompanied by a development of heat, the compound containing, therefore, less energy than the components, the opposite is here the case. One must not, therefore, assume that every process of combination takes place with evolution of heat: the reverse is also possible, although less frequent.

If we write the two equations

$$2H_2 + O_2 = 2H_2O + 572\ kj$$

and

$$2H_2O + O_2 = 2H_2O_2 - 194\ kj$$

below one another and add, we obtain

$$2H_2 + 2O_2 = 2H_2O_2 + 2 \times 189\ kj.$$

Expressed in words, this equation reads: In the combination of oxygen and hydrogen to form hydrogen peroxide, 189 *kj* are developed for every mole.

In this way we obtain the heat of reaction of a process which cannot be carried out in such a way that it can be measured, and which, therefore, cannot be directly investigated. The justification for this calculation lies in the fact that every formula in a thermochemical equation represents a definite amount of energy, and in the fact that energy magnitudes can be added without limit. The calculation, therefore, presupposes nothing more than the validity of the law of the conservation of energy.

On subtracting the upper equation from the lower we obtain

$$2H_2O_2 + 2H_2 = 4H_2O + 2 \times 383\ kj.$$

That is: on the combustion of hydrogen to water by means of ydrogen peroxide, 383 *kj* pro mole of peroxide are evolved. Here, gain, the heat effect of a reaction has been calculated which cannot e subjected to direct measurement.

As can be seen from these calculations, one can, on the basis of a ew measurements, calculate the heat effect of quite a number of eactions which take place or could take place between the reacting ubstances. The number of calculations possible increases very rapidly ith the number of direct measurements. There is a whole branch of scientific chemistry, known as *thermochemistry*, which has the study of these relations for its object.

These calculations can be most readily reviewed, if for each compound the (positive or negative) heat effect which accompanies or would accompany its formation *from its elements* is calculated. This is called the *heat of formation*. The heat of formation of water is equal to 286 *kj*; that of hydrogen peroxide, 189 *kj*.

In the sequel we shall give the heats of formation of the most important substances so far as they are known; from them there can then be calculated the heat effects of the other reactions in which these substances take part.

CHAPTER IX

CHLORINE

Formation from Hydrochloric Acid and Oxygen.—We now turn to the study of hydrochloric acid, which was used (p. 85) in the preparation of hydrogen. From those experiments it followed that hydrogen is one of its constituents. It contains, besides, another

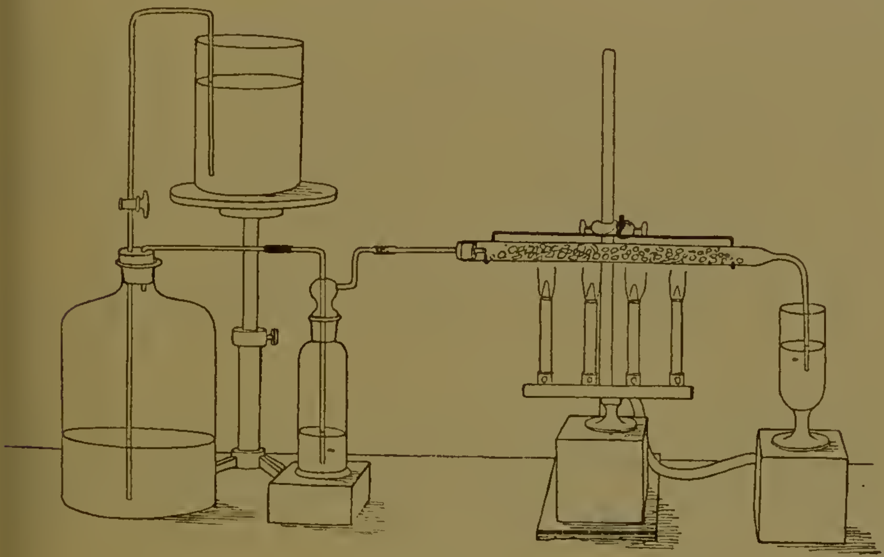

Fig. 58.

lement called *chlorine,* which in that experiment did not become isible because it united with the zinc, for which very reason, indeed, ydrogen was formed.

To obtain this other element we must proceed in the reverse nanner: to set free the chlorine, we must convert the hydrogen into compound which can be separated. This we can effect by acting on ydrochloric acid with *oxygen.* If this action took place in the desired ay, hydrochloric acid plus oxygen would pass into water plus chlorine, nd we should attain our object.

As a matter of fact this process is practicable. If a current of air be passed through a bottle filled with concentrated hydrochloric acid and slightly warmed, vaporisation takes place and a mixture of air and hydrochloric acid is produced (Fig. 58). This is passed through the tube B filled with pieces of pumice-stone. For a reason to be given immediately, the pumice-stone has been moistened with a solution of copper sulphate and ignited. When the apparatus is set working, there escapes from the tube a mixture of air, aqueous vapour, and a new substance which betrays itself by an exceedingly unpleasant smell. This substance further possesses the property of giving a conspicuously dark-brown colour to a solution of potassium iodide (p. 47). Paper dyed with vegetable colours, *e.g.* litmus paper, is bleached, and the bright surface of all kinds of metals, even silver and mercury, becomes tarnished. This new substance is the sought-for element, chlorine.

The amount of chlorine obtained in this way is small. Furthermore, the substance is contaminated by the excess of air, so that this method is not suitable for the preparation of chlorine for laboratory purposes, and was mentioned first only on account of the simplicity of the process.

The object of the copper sulphate on the pumice is to accelerate the interaction between the hydrogen chloride and the air, for the copper sulphate acts catalytically on this reaction in a manner similar to that in which platinum acts towards detonating gas (p. 103).

This method for obtaining chlorine from hydrochloric acid and air is carried out on a large scale for technical purposes, and is called, after its elaborator, the *Deacon process.*

Another Preparation of Chlorine.—Better yields and a purer product are obtained by employing for the transformation of the hydrochloric acid suitable oxygen compounds instead of the gaseous oxygen of the air. As such, there can be used most of those substances which we have already got to know as sources of oxygen. The most suitable is pyrolusite, which is a compound of manganese (p. 54) rich in oxygen. Manganese is a metal similar to iron, which occurs in large quantities in nature and finds manifold application in the arts.

The flask *A*, Fig. 59, contains pyrolusite in coarse lumps and is gently warmed on the water-bath. The hydrochloric acid is contained in the dropping-funnel *B*, by which means the acid can be allowed to flow to the pyrolusite as required. The evolved gas is led away through the tube *C*, washed with water in *D* to remove the hydrochloric acid present, and dried with sulphuric acid in *E*.

A still more convenient method for obtaining chlorine depends on the use of *bleaching-powder*, since this substance gives a copious evolution of chlorine, even in the cold, when treated with hydrochloric acid. For this method a simple bottle is used, partly filled with bleaching-powder and furnished with a dropping-funnel, in which the concentrated hydrochloric acid is placed. The evolution of gas takes place in proportion as the acid is allowed to flow to the bleaching-powder.

The theory of this process cannot be given till later (Chap. XXIII.); it must suffice here to indicate that we are again dealing with an oxidation of the hydrochloric acid, the hydrogen of this being converted into water.

Properties of Chlorine.—By these methods a gaseous substance is obtained of a yellowish-green colour, which is distinguished by very striking properties from all the gases hitherto studied. It possesses in the highest degree the unpleasant smell we have already mentioned, has a corrosive action on the mucous membrane of the mouth and nose, and is therefore very harmful and poisonous. This gas cannot, like oxygen or hydrogen, be collected over water, since it is fairly soluble in that liquid. In other cases mercury is used for such gases, but it cannot be employed here, since it immediately combines with chlorine. In order to collect the gas, use is made of its great density; if the gas is conducted to the bottom of a dry bottle, it remains at the bottom and gradually displaces the air. By holding a piece of white paper behind the bottle, it is easy to observe the progress of the filling, the green gas forming a distinct contrast to the colourless air. When the bottle is filled, it is closed by a ground-in stopper, rendered tight with vaseline, and the filling of a fresh bottle is proceeded with.

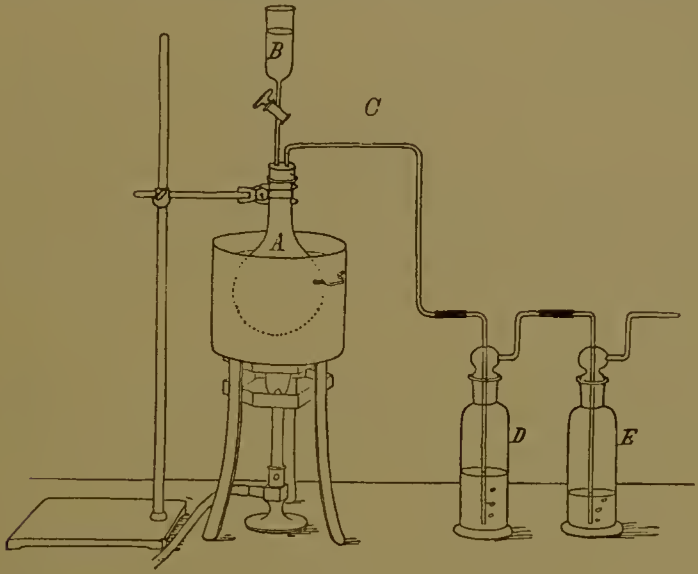

FIG. 59.

Since some chlorine always escapes into the air during this process, the preparation must be carried out in a good-drawing fume chamber, or else in the open air. Also, while the bottle is being filled, it may be closed by a doubly bored cork through which a supply and a discharge tube pass. By means of a wash-bottle with caustic soda, it is then possible to render the escaping gas innocuous.

As is seen from this behaviour, the density of chlorine gas is considerably greater than that of air; its molar weight has been found by measurement to be 71. Chlorine is, therefore, about 2·3 times as heavy as oxygen (M.W. = 32), and 2·5 times as heavy as air.

Chlorine is distinguished from the gases hitherto considered, by the fact that it obeys the gas laws with much less exactness. Like all gases of comparatively great density, it exhibits measurable deviations even under ordinary conditions; for with increase of pressure or fall of temperature its density increases more than it ought to, according to the gas laws.

Connected with this is the fact that chlorine can be fairly easily condensed to a liquid. At 0° a pressure of 3·7 atmospheres is sufficient for this; at room temperature (18°) the pressure amounts to 16·5 atmospheres, and the critical temperature is reached only at 146°. Above this temperature chlorine cannot be converted into a liquid by any pressure. The highest pressure just underneath this temperature by which chlorine can still be liquefied, *i.e.* the critical pressure, amounts to 94 atm.

These properties, then, make it possible to condense chlorine into steel bottles which have been tested for a considerably higher pressure than the critical pressure, and in which the chlorine can be stored and transported. Although chlorine under ordinary conditions, especially when moist, eagerly combines with almost all metals, carefully dried chlorine shows itself so inactive that there is nothing to prevent its manipulation in metallic vessels. By means of an adjustable cock the gas can be withdrawn from such a holder (Fig. 37, p. 103) as desired, and one is thereby spared the very troublesome preparation of the gas when much of it is required.

The peculiar action which water here exhibits is not limited to chlorine; there are very many reactions which take place only in the presence of water with such velocity that the result can be observed in a measurable time. All these must be numbered along with the *catalytic phenomena* (p. 104).

Liquid chlorine has the green-yellow colour of the gas in a much higher degree. It is an oily liquid, of density 1·56.

At lower temperatures chlorine passes into a solid, crystalline substance which exhibits the same green-yellow colour as is shown by chlorine in its other states.

Solubility in Water.—Chlorine dissolves in water in fairly large amount; under ordinary circumstances one litre of water absorbs about three litres of chlorine. The solution, which has the smell and taste, as well as the corrosive and bleaching properties, of chlorine gas is called chlorine water, and is used for chemical and medical pur poses. As is the rule with gases, more chlorine is dissolved at a lower temperature than at a higher.

More exact investigations into the condition of chlorine in aqueous solution have shown that it is not a case of simple solution, but that chemical reactions take place between the chlorine and the water. We can enter into this more fully only after the other compounds of chlorine have been described.

Decomposition of Chlorine Water in Light.—Chlorine water must be kept protected from the light, since it undergoes a remarkable decomposition under the influence of illumination. The chlorine then combines with the hydrogen of the water to form hydrogen chloride or hydrochloric acid, and oxygen is set free. In strong sunlight this reaction takes place so quickly in saturated chlorine water that the liquid sparkles like soda-water. If the gas is collected, one can easily convince oneself of its chemical nature by the bursting into flame of a glowing splinter.

Actions of this kind, whereby chemical processes are brought about or accelerated by the influence of light, are called *photochemical*, and the science which studies them is called *photochemistry*. These processes are of very great general and technical importance. On the one hand, the processes by means of which green plants build up their structures depend on photochemical phenomena, as can be seen from the fact that the plants cannot grow when the light is shut out. On the other hand, photochemical processes are turned to practical account in photography, which, along with the arts dependent on it, has now obtained an extensive application in the most varied departments of work.

* The action of light on the decomposition of chlorine water should probably be interpreted as an acceleration of a process which of itself takes place very slowly, for the reaction occurs also to an appreciable extent in darkness, and the chemical equilibrium is such that dilute hydrochloric acid and oxygen represent a more stable system than an aqueous chlorine solution.

* The different kinds of light do not act equally strongly on chlorine water; the red rays are found to be almost without effect, whereas the blue and the violet, as well as the invisible rays of still shorter wave length, the *ultra-violet* rays, exhibit a much greater activity. Similar relations are observed in many other cases of photochemical action. It would, however, be incorrect to regard the rays of short wave length as being, therefore, specially active chemically. The region of rays in which the greatest chemical activity is manifested is entirely dependent on the chemical process influenced by the light. In particular, the most important photochemical process, the assimilation in green plants, proceeds with greatest energy in yellow and red light.

* On comparing the process under discussion with that described

on p. 166), where chlorine and water were produced from hydrochloric acid and oxygen, a contradiction seems to be contained in the foregoing statement, for in that case exactly the opposite reaction took place, and chlorine in contact with water formed a more stable system than hydrochloric acid and oxygen. The difference lies in the fact that in the former case we were dealing with *gaseous* hydrogen chloride, but here with a *dilute aqueous solution* of it. The stability of a compound is frequently much greater in solution than in the pure state, and chemical reactions can, therefore, readily undergo reversal, according as the one or the other condition obtains.

Chlorine Hydrate—The Phase Law.—When gaseous chlorine is passed into ice-cold water—it is best to have some pieces of ice floating in the liquid—a greenish crystalline substance soon separates out. This consists of chlorine and water according to the formula $Cl_2 + 8H_2O$, and is called *chlorine hydrate*. Under atmospheric pressure this substance is stable only up to + 9·6°; if heated to a higher temperature it decomposes into chlorine, which escapes as a gas, and water (saturated with chlorine), which remains behind. If the pressure be increased, chlorine hydrate can be kept at still higher temperatures; if it be lowered, the temperature of stability of the hydrate becomes lower. There corresponds to each temperature, therefore, a definite pressure of the chlorine gas, at which the hydrate can exist.

These relations show the greatest similarity to those existing in the case of a volatile liquid (p. 119), where the possibility of liquid and vapour existing side by side is also associated with a definite pressure, which increases with rising temperature but is independent of the relative or absolute amounts of the two forms. In this case also, the existence of chlorine hydrate in contact with gaseous chlorine and solution is regulated only by a relation between pressure and temperature, and the quantity relations have no influence.

A difference exists here, however, in so far as, in the condition of equilibrium, there are present, not two phases (p. 128), but three, viz. chlorine hydrate, saturated aqueous solution of chlorine, and gaseous chlorine. This is due to the fact that we are not now dealing with the equilibrium of a single substance, as in the case of water, but with two substances, water and chlorine. In the same measure as the number of substances increases, the number of phases which can exist side by side also increases.

Just as water along with vapour or along with ice, *i.e.* two phases of water, can exist side by side at *different* temperatures, but three phases, viz. water, vapour, and ice, only at *one single* temperature, so in the present case there can exist three phases side by side at different temperatures, and there must be a single point at which four phases can be present. Such a point is got when we assume ice as fourth phase. As a matter of fact, ice, chlorine hydrate, chlorine water, and chlorine gas can exist side by side at the temperature −0·24°. This possibility, however, is restricted to this one temperature: if the temperature be raised, the ice disappears and three phases remain; if the temperature be lowered, the chlorine water disappears, passing into ice and chlorine hydrate, and again three phases are left.

The *pressure* also, as well as the temperature, is definite at this point. It amounts to 24·4 cm. If it be increased, the gaseous chlorine disappears; if it be reduced, one of the other phases disappears.

All these relations are quite similar to those obtaining for one substance, only the number of the phases has been increased by one, by which number, also, the components have been increased. We are here dealing with a quite general law, which was established by W. Gibbs. This "phase law" is expressed by the formula

$$P + F = C + 2.$$

In this formula, P denotes the number of the phases, F the degrees of freedom, in the sense given on p. 128. C is the number of the components in the system considered. In the case of *one* component the sum of the phases and the degrees of freedom is three, *i.e.* one-phase systems have two, two-phase systems one, and three-phase systems no degrees of freedom, as has been shown in the case of water (and of every other substance which can occur in different states). In systems of two components four phases are required to produce a system with no degrees of freedom, and every three-phase system has one degree of freedom; in water and chlorine we have just had an example of this. In what follows we shall find manifold application of this important law.

Chemical Properties of Chlorine.—Chlorine is a substance of great chemical activity, and, unlike oxygen, manifests this even at ordinary temperatures. This is not due to a much greater amount of energy becoming available when chlorine acts on other substances than when the corresponding processes take place with oxygen; on the contrary, it is pretty much the same in both cases. The greater chemical activity of chlorine is rather to be attributed to the greater velocity with which its reactions proceed at ordinary temperatures, compared with those of oxygen.

One can convince oneself of this readiness to act by means of combustion experiments which are quite similar in appearance to those with oxygen, in which, however, the other substances do not require to be first ignited. On the contrary, they ignite spontaneously.

Thus, a ball of Dutch metal (which consists chiefly of copper) or of thin copper-foil, immediately becomes incandescent when thrown into a bottle containing chlorine, and the chlorine compound of copper is formed. The metal antimony forms a rain of fire when allowed to fall in the form of a fine powder into chlorine. Phosphorus introduced into chlorine likewise ignites spontaneously, and burns with a livid flame forming a greenish-white solid substance which settles on the sides of the bottle.

Combustion without Oxygen.—We have here phenomena which show all the characteristics of the combustions in oxygen gas. From this we must therefore draw the conclusion that combination with oxygen is not necessary for combustion in the wider sense. On the contrary, other chemical processes can give rise to these phenomena if they take place with sufficient velocity, and with the development of so much heat that the products of reaction are thereby raised to incandescence, *i.e.* to at least 500°.

If gaseous substances or vapours are formed in the reaction, we obtain the phenomenon of flame which is formed by the incandescent gas; otherwise, one sees only incandescent liquid or solid masses, as in the case of the combustion of iron (p. 64).

If one bears in mind what was said on p. 65 concerning rapid combustion, it will be at once seen that the characteristic phenomena in the case of the action of chlorine depend on the fact that even at ordinary temperatures the velocity of the chemical processes has a large value.

Sub-Chlorides and Chlorides.—In a manner similar to the cases already mentioned, chlorine is able to combine with most of the elements. The metals, especially, are capable of yielding such compounds. The names of these compounds are formed by adding the word chloride to the name of the other element; thus, copper chloride, antimony chloride. By this nomenclature we can, when the chlorine is capable of forming different compounds with the same element, distinguish several degrees. In this case the compound containing less chlorine is called *sub-chloride;* that containing more chlorine, *chloride.*[1] If still more stages have to be expressed, the lowest is designated proto-, and the highest super-, hyper-, or perchloride.

Of the different compounds which can be formed from chlorine we shall mention still one example. If the metal sodium is placed in a tube through which a current of chlorine is passing, and is gently warmed, the two elements combine with great energy and with great development of heat. The product of the reaction is a white crystalline substance, which is readily soluble in water, has a saline taste, and can in no way be distinguished from *common salt.* The chemical name for common salt must therefore be sodium chloride, since it is formed from the elements chlorine and sodium.

Chlorine and Hydrogen.—One of the most important compounds of chlorine is that with hydrogen. If a jet of hydrogen gas be ignited and the flame introduced into a cylinder with chlorine (Fig.

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[1] In English, it is customary to express these relations by the terminations -ous and -ic affixed to the name of the metal. Thus, copper sub-chloride is called cuprous chloride, and the higher chloride, cupric chloride. Similarly also, mercurous chloride and mercuric chloride, ferrous chloride and ferric chloride, etc.—Tr.

60), the hydrogen continues to burn; only the colour of the flame changes from blue to a whitish green. The combustion continues some time, but the flame finally goes out and the greenish colour of the chlorine in the cylinder has now disappeared. In its place is a colourless gas which, in contact with the moist air, forms a dense, white mist, and is much more readily absorbed by water than chlorine. If the cylinder is rinsed out with water, a liquid with a strong acid taste is obtained, which does not bleach blue litmus paper, as chlorine does, but changes the colour to red.

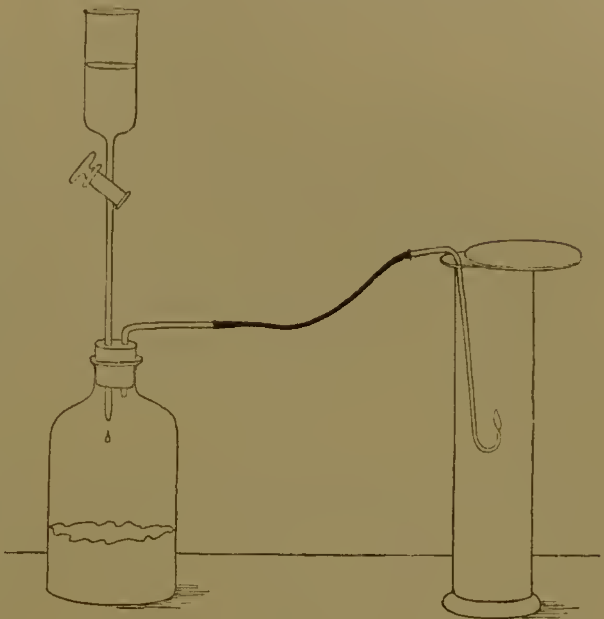

Fig. 60.

It can be conjectured what is produced in the combustion of chlorine and hydrogen. Hydrochloric acid we already know to be a substance from which chlorine and hydrogen can be obtained; accordingly, hydrochloric acid is to be looked for as the product of the interaction of these two gases.

As a matter of fact, the same properties are shown by the aqueous solution of the product of combustion as by hydrochloric acid. In a dilute state it has a strong acid taste and reddens litmus paper. It is true that there are a number of other substances which also have these properties; still one can satisfy oneself by means of reactions which are given only by hydrochloric acid, that hydrochloric acid is, indeed, the only substance formed in the combustion of hydrogen in chlorine.

Indirect Formation of Hydrochloric Acid.—The compound of chlorine with hydrogen can be formed not only when the latter element is present in the free state, but also in very many cases by the action of chlorine on compounds containing hydrogen.

An example of this has already been given in the decomposition of water by chlorine under the influence of light (p. 169). A similar process is seen in a more striking manner by introducing a piece of paper moistened with turpentine into a bottle of chlorine. Turpentine consists of hydrogen and carbon; with the former, chlorine combines after a few moments with evolution of much heat and the production of a dark-red flame. At the same time, the carbon separates out as a black soot. That hydrochloric acid has been formed in this reaction, is found on washing out the contents of the bottle with water; these exhibit exactly the same properties as were shown by the product of the combustion of hydrogen in chlorine.

The burning of a wax candle in chlorine depends on the same relations. Wax also consists chiefly of hydrogen and carbon (along with some oxygen). If a burning wax candle be introduced into a bottle of chlorine, it continues to burn; at the same time, however, the flame becomes dusky red in colour and emits large quantities of soot or carbon, since the chlorine cannot, under these conditions, combine with the carbon. In this case, also, the formation of hydrogen chloride can be easily demonstrated.

Some of the important technical applications of chlorine depend on its power of withdrawing hydrogen from substances containing it and therefore destroying them, *i.e.* converting them into other substances.

On the one hand, chlorine is used for bleaching. The vegetable fibres from which textile fabrics and paper are made are generally not colourless, as it is desirable they should be for use or for being further dyed, but contain natural dyes which must be removed from them. For this purpose they are treated with chlorine, which removes hydrogen from the dyes and converts them into other, non-coloured compounds.

Along with this dehydrogenising action, *oxidation* takes place by means of the chlorine. This depends on the co-operation of water, which, as we have already seen, is decomposed by chlorine with elimination of oxygen. If this process takes place in the presence of other substances which can form oxygen compounds, these are formed with special readiness, *i.e.* the substances are oxidised.

On the other hand, chlorine is used for disinfecting and sterilising. This action also depends on the withdrawal of hydrogen from or the oxidation experienced by malodorous and other harmful substances through the agency of chlorine. Especially is chlorine a violent poison for the small living organisms by whose activity rotting, putrefaction, and such like, are caused, and which play a part in the spread of certain diseases. The application of chlorine for such purposes is, unfortunately, very greatly limited by the fact that it is also a very harmful substance for the higher organisms, and on somewhat more prolonged action can give rise to serious symptoms.

Composition of Hydrogen Chloride.—The combination of chlorine with hydrogen is, likewise, subject to the law of Gay-Lussac regarding the volume ratios in the interaction between gases (p. 139). In fact, chlorine and hydrogen combine in *equal* volumes, and the hydrochloric acid gas formed occupies the same volume as was previously occupied by the mixed gases. Whereas, therefore, there was, in the formation of water vapour, a diminution from three volumes to two, we have in the present case a combination without change of volume. The molar weight of hydrochloric acid gas is therefore obtained as the half of the sum of the molar weights of chlorine and hydrogen. This calculation is, in numbers,

$$Cl_2 + H_2 = 2HCl$$
$$70{\cdot}90 + 2{\cdot}02 = 2 \times 36{\cdot}46.$$

One can convince oneself of these relations, both by the decomposition of hydrogen chloride, that is, by *analysis*, and by the formation of hydrogen chloride from its elements, that is, by *synthesis*.

When an electric current is conducted through hydrochloric acid by means of two platinum plates, chlorine appears at the one plate, and hydrogen at the other. The energy which was set free on the formation of the hydrogen chloride from chlorine and hydrogen and on the solution of the hydrochloric acid gas in water, is again given back by the electric current, which therefore makes it possible for the two elements to separate in the free state. The details of this process will later form the subject of exhaustive consideration; at this point, we rest satisfied with the result that the hydrochloric acid is decomposed by the electric current, and that its elements are evolved separately.

This experiment is performed in the apparatus shown in Fig. 56, on p. 138. On starting the process by passing the electric current, after the apparatus has been filled with strong hydrochloric acid, gas is at first seen to be evolved only at one electrode; this gas is hydrogen. At the other electrode there is only a yellow-green coloration produced, because the chlorine evolved dissolves in the hydrochloric acid. Gradually this becomes saturated with chlorine and gas is evolved regularly at both plates, or "electrodes."

After the first portions of gas have been allowed to escape, by opening the taps, it is easy to satisfy oneself that the two limbs of the apparatus become simultaneously filled with equal volumes of gas, and that, as a matter of fact, therefore, equal volumes of the two gases are produced in the decomposition of hydrochloric acid.

That one of the gases is hydrogen, is shown by the fact that it burns with a blue flame in the air. The other gas can be recognised as chlorine, even by its colour; the smell and the bleaching action on a piece of litmus paper, confirm this.

Formation of Hydrogen Chloride from its Elements.—If, on the other hand, a mixture of equal volumes of chlorine and hydrogen is prepared, it can be ignited by an electric spark in the same way as detonating gas, and is completely converted, with explosion, into hydrochloric acid. In this case, however, there are some remarkable phenomena to be observed.

It is not only by rise of temperature that a mixture of equal volumes of chlorine and hydrogen, which, on account of the similarity mentioned, is called chlorine detonating gas, passes into hydrogen chloride; *light*, also, has the property of bringing about this combination. Weak light, such as subdued day-light in a room, acts rather slowly; strong light, such as the rays of the sun, produces such rapid action that a violent explosion takes place.

The experiment can be carried out in the following manner. A white glass bottle is filled, in the ordinary way, with chlorine, and another of equal capacity, with hydrogen. After the removal of the corks from both bottles, the one containing hydrogen is placed, mouth downwards, on the bottle containing chlorine. This operation must be carried out in a room illuminated only by a candle standing at some distance. To ensure a more air-tight junction, an indiarubber ring can be placed between the two bottles and, for convenience of manipulation, these can be clamped together in a frame (Fig. 61). By inverting the bottles several times, the contents are mixed; the bottles are then separated, closed with the corks and wrapped in black paper or placed in light-tight, cardboard cases.

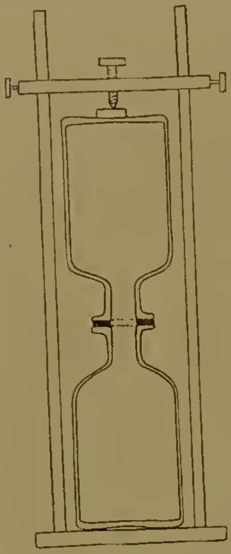
Fig. 61.

If one of these bottles be now placed in direct sunlight, taking care that no harm can be done by the glass splinters which fly about, a violent explosion takes place. If, on the other hand, the other bottle be allowed to stand uncovered in a corner of the room, not too brightly illuminated, no change, apparently, takes place in it. After some time, however, varying according to the strength of the light, the green colour of the chlorine disappears and the contents of the bottle appear colourless. If, now, the neck of the bottle be placed under mercury and the cork removed, neither does gas pass out nor mercury enter, which shows that the combination of the two gases has taken place without change of volume.[1]

If the bottle be now placed over water, the latter dissolves the hydrogen chloride and rushes with great rapidity into the bottle. As a rule, a small gaseous residue is left, because, under the conditions of the experiment, it is not possible either to have the gases quite pure or exactly in the proper proportions. That hydrochloric acid has been produced, is shown by the water having an acid taste and reddening blue litmus paper.

Electrolytic Preparation of Chlorine Detonating Gas.—The same relations can be observed in a more convenient manner and independently of sunlight, as follows. Concentrated hydrochloric acid is decomposed by the electric current in the vessel A (Fig. 62), which is furnished with two electrodes of carbon (thin arc-light carbons), or of platinum. Under these conditions the gases produced immediately mix and, after the evolution has been going on for half or a whole hour, in the right proportions. In the bulbs which are blown on the delivery tube, there are a few drops of water, to free the gases from the hydrochloric acid which they carry over. Attached to the delivery tube is a series of glass bulbs blown out of thin glass and connected by thin-walled capillaries; they may be 4 to 6 cm. in diameter. These are filled with the explosive mixture by displacement. Since this is heavier than air, the row of bulbs is placed in an upright position and the gas passed in at the foot. All this must be done in a weak light, with exclusion of daylight; for this purpose the light is most conveniently supplied by a lamp with yellow cylinder, such as is used for photographic purposes. After the gas has been passing for at least half an hour, precautions being taken to carry off the excess, the two ends of the row of bulbs are closed, for the time being, with wax; one then proceeds to melt off the bulbs from one another.

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[1] Sometimes, if the gases were not dry, some mercury passes into the bottle, part of the hydrochloric acid which was produced having dissolved in the water present. It is necessary, therefore, to see that the gases are dry, and the simplest way is to fill the bottle with hydrogen also by displacement, the bottle being inverted and gas passed in through a tube reaching to the top.

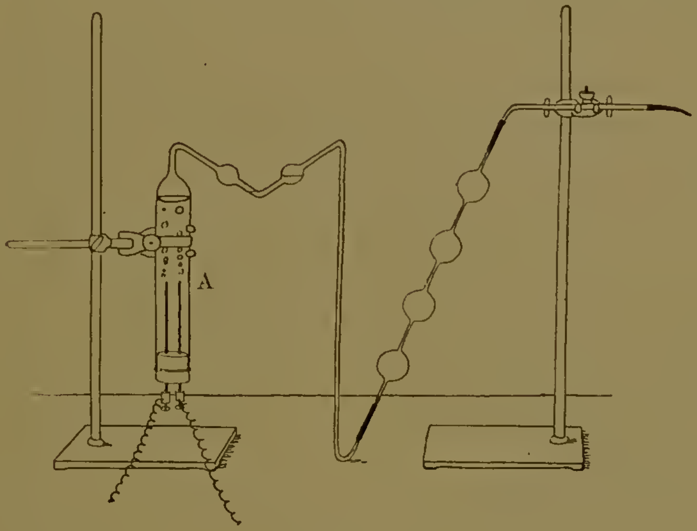

Fig. 62.

Although the chlorine detonating gas can be caused to explode by heat, the capillaries can, without danger, be softened in a small gas flame and closed by drawing out. The gas which is directly heated burns, certainly, to hydrochloric acid, but the combustion does not pass into the bulbs, because the heat which is developed is taken up by the glass walls of the tube.

With the bulbs of chlorine detonating gas prepared in this way, the experiments described can also be carried out: the explosion of these is unattended with risk, since the light glass splinters can scarcely do any damage. Instead of sunlight, burning magnesium can be used to bring about the explosion: either magnesium powder is placed in a glass tube 1 cm. wide and blown into a flame, or a lamp is employed such as is used in taking flash-light photographs.

Photochemical Actions.—It follows from the experiments described, that the action of light on the chlorine detonating gas, similarly to that on chlorine water (p. 169), consists in increasing the velocity of combination of the two components. It has been repeatedly explained that there is reason to suppose that in every system in which a chemical process can take place, that process really does take place, although often only with an immeasurably small velocity. In the case of the chlorine detonating gas, also, we may make such an assumption, and the action of light consists in increasing this immeasurably small velocity to a measurable one.

In fact, it has been shown by appropriate investigations, that the velocity of transformation of the chlorine detonating gas into hydrochloric acid is proportional to the strength of the light acting.

* The manner of this action is still somewhat obscure. We must by no means assume that the energy of the light is expended in bringing about the reaction. No energy is consumed in the combination of the gases; on the contrary, a fairly large amount of energy is set free, as follows from the phenomena of explosion, and the spontaneous transmission of the combustion through a tube at the end of which it is initiated. From the observation that completely dry chlorine detonating gas is scarcely sensitive to light, combined with some other facts, it becomes probable that we are dealing here with a rather complicated process which takes place with the co-operation of the elements of water.

Hydrochloric Acid.—Hydrochloric acid is met with in commerce as a liquid like water, which, in the pure state, is colourless; the crude hydrochloric acid, however, is generally coloured yellow through contamination with iron. This is not the pure compound hydrogen chloride, but a solution of it in water. Pure hydrogen chloride is a gas, and as such is difficult to employ and to transport. A solution of it in water, containing rather more than a third of its weight of hydrogen chloride, is therefore used. Solutions containing this amount or more of hydrogen chloride fume in the air, gas being given off; solutions containing less than 20 per cent of hydrogen chloride no longer fum at the room temperature.

In order to obtain pure hydrogen chloride gas from its solution, commercial hydrochloric acid, it is necessary to withdraw the wate from the latter. We have already learned that concentrated sulphuri acid can be used for such purposes. Accordingly, our apparatus consists of a bottle through the cork of which pass a dropping-funnel an delivery tube. The tube of the dropping-funnel, which is filled wit fuming hydrochloric acid, is drawn out to a narrow point and reache to the bottom of the flask. If the tap be opened and the hydrochlori acid allowed to pass slowly into the sulphuric acid, the water is taken up by the latter and the hydrogen chloride escapes as a gas.

The upper part of the generating flask does not become coloured; hydrogen chloride is, therefore, colourless. It cannot be collected over water, nor can it be collected well by displacement, since it is only slightly heavier than air. It can, however, be collected over mercury, since this is not attacked by hydrogen chloride when both substances are pure.

* The use of mercury for collecting such gases as are readily dissolved by water is due to Priestley (1780), and was, at the time, an important invention, since it directly led to the knowledge of quite a number of gases which are dissolved by water, and of which, therefore, one could previously know nothing. The mercury trough which is used in such operations is generally made of porcelain, and of such a form that the quantity of this rather expensive metal required to fill it is as small as possible.

Properties of Hydrogen Chloride.—Hydrogen chloride is a colourless gas, the density of which amounts to 36·5, corresponding to the formula HCl. It is, therefore, a little heavier than air. By pressure and cold, it can be converted into a liquid; at $-113°$ it solidifies. The liquid boils under atmospheric pressure at $-80°$; its pressure at $0°$ amounts to 2·8 atm.

Liquid hydrogen chloride is a colourless, rather indifferent liquid, exhibiting little of the chemical reactivity which can be observed in the case of its aqueous solution. The liquid neither acts on metals, nor reddens litmus, nor, when water is carefully excluded, does it show any of the other properties of acids. This remarkable contrast to the behaviour of the aqueous solution has great significance and will be explained later.

Of the other properties of hydrogen chloride the most striking is its great solubility in water. At room temperature, one volume of water absorbs 450 volumes of the gas. By the absorption, a large quantity of heat is developed, which points to a reaction between the water and the hydrogen chloride gas. This reaction is of a special kind, and will be discussed more fully at a later point.

The great solubility of hydrogen chloride in water can be shown by blowing a little water up through the mercury to the gas collected in a cylinder, by means of a pipette bent at the lower end. The mercury immediately ascends and, if the gas is pure, again fills the cylinder. There generally remains, it is

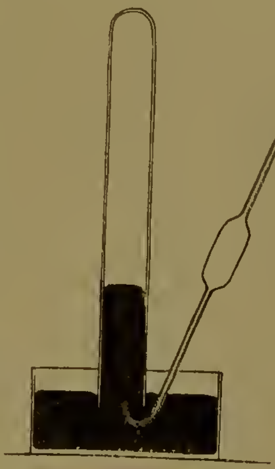

Fig. 63.

true, a bubble of air unabsorbed, since it is very difficult to remove the last traces of foreign gases.

The water which was added has been converted, by the absorption of the hydrogen chloride, into hydrochloric acid. If a piece of metallic magnesium be introduced under the mercury and allowed to pass up to the hydrochloric acid, it decomposes this, combining with the chlorine and liberating the hydrogen. When the evolution of gas has ceased, it is easy to convince oneself that the gas is hydrogen and that its volume is half that occupied by the hydrogen chloride gas.[1]

Absorption of Hydrogen Chloride by Water.—In passing hydrogen chloride gas in comparatively large quantity into water for the purpose of preparing aqueous hydrochloric acid, some precautions must be observed on account of the violence of the absorption. The apparatus used for this purpose is shown in Fig. 64. The hydrogen chloride gas is generated in *A*; *B* is an empty wash-bottle, and *C* a wash-bottle half filled with water. The two wash-bottles are connected up opposed to one another, so that in *B* the gas enters through the short and escapes through the long tube; *C*, in the reverse manner, receives the gas through the long tube. When the gas is evolved, it first fills the empty bottle *B*, and then passes over into *C*, where it is absorbed by the water; the admixed air escapes through the short tube. If, now, for any reason, the evolution of gas should cease, the water would, if the bottle *B* were not there, pass back into the generating flask *A*, on account of the absorption of the gas; by the action of the water on the concentrated sulphuric acid, an explosion might result, and, in any case, the experiment would be spoiled. The bottle *B* guards against this contingency. If regurgitation should occur, the water cannot get further than *B*, and if the pressure in *A* is further

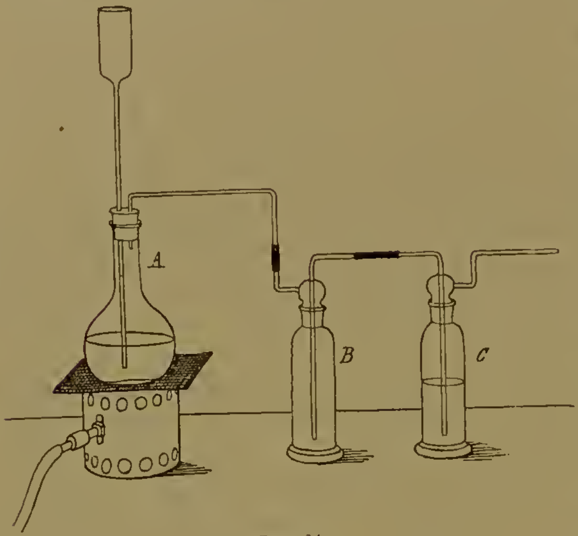

FIG. 64.

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[1] To ensure the success of the experiment, the apparatus must be previously carefully dried, as, otherwise, the volume of the hydrogen chloride, on account of its great solubility in water, appears too small. Also, one must not omit to bring the gas under the same pressure as at the commencement of the experiment. This is most simply accomplished by closing the cylinder under mercury, placing it in a large vessel of water, and sinking it until the level of the water outside and inside is the same. It is here presupposed that in measuring the hydrogen chloride over mercury, that gas also was under atmospheric pressure.

reduced, air passes from C through the liquid in B. When the pressure in A again rises, the liquid is first forced over from B into C again, and the absorption goes on regularly.

Besides the one described, there are many other safety arrangements to prevent the liquid passing back into the generator. One of the simplest of these consists in inserting an open funnel tube in the cork of the generator itself (Fig. 64). It will be easy for the reader himself to work out the action of this in the case of diminished pressure.

When somewhat larger quantities of hydrogen chloride are dissolved in water, the temperature of the solution rises to an undesirable height, owing to the heat developed in the process. The solution is therefore cooled by placing the bottle in cold water or surrounding it with ice.

In the commercial preparation of hydrochloric acid, the hydrogen chloride is, of course, not prepared by the method employed by us. It is obtained by the action of sulphuric acid on common salt, according to a chemical reaction, the theory of which cannot be developed till later (Chap. XII.).

Hydrogen Chloride and Water.—Most gases dissolve in water to a much less extent than hydrogen chloride, and the absorption follows a law discovered by Henry, which states that the amount dissolved is proportional to the pressure. In the case of hydrochloric acid, this law is not even approximately fulfilled ; on the contrary, the greater portion of the gas is absorbed independently of the pressure, and an increase of pressure effects only a small increase in the amount dissolved.

This behaviour points to the fact that in the case of the absorption of hydrogen chloride a special chemical process also takes part. This process consists *in the elements of hydrogen chloride passing, in aqueous solution, into another condition.* It is very remarkable that anhydrous liquid hydrogen chloride does not exhibit the properties of an acid (p. 179), although it contains the elements of one. This is due to the fact that the characteristic properties of acids are not exhibited by the components of hydrogen chloride until this is converted, through solution in water, into the other condition.

When, therefore, hydrogen chloride is dissolved in water, two processes occur. One portion of the acid, which is all the greater the more dilute the solution, passes into the new condition ; another portion dissolves unchanged as hydrogen chloride. The first portion does not follow Henry's law of the absorption of gases, but only the second. For this reason, the amount absorbed increases more slowly than the pressure.

There is a further remarkable phenomenon connected with this. Hydrogen chloride, in the pure state, boils at − 102° under atmospheric pressure ; water boils at + 100°. One would suppose, therefore, that the boiling points of aqueous solutions of hydrochloric acid would lie between these two temperatures. This, however, is the case only for very concentrated solutions; more dilute solutions, on the other hand, boil at a higher temperature than water, so that by the addition of the very volatile substance to water, the volatility is not increased but diminished.

The relation between composition and boiling point is represented by the curve (Fig. 65), in which the percentage content of hydrogen chloride is measured on the horizontal axis, and the boiling points under atmospheric pressure on the vertical. As can be seen, the curve reaches a maximum at 110°, corresponding to a 20% solution, and all other mixtures boil lower than the 20% acid.

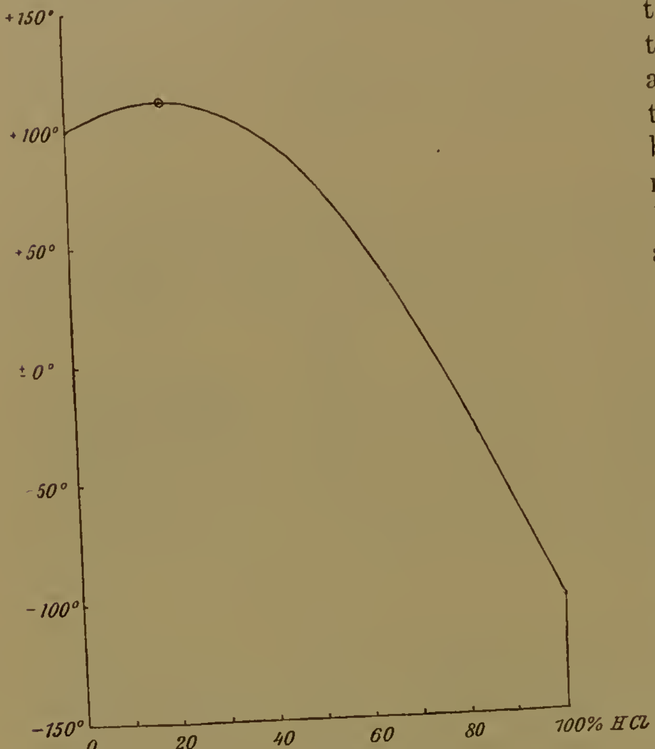

Fig. 65.

This fact causes the following behaviour on distillation. We premise that, on distillation, the composition of a mixture can evidently change only in such a way that the boiling point *rises*, for the more volatile, *i.e.* the lower boiling portion, must pass over first, and the residue must therefore, necessarily, boil higher than the original mixture. If now the strength of the acid solution is below 20%, lower boiling, more dilute acid must distil over, and a stronger, higher boiling acid remains behind. This continues until the residue contains 20% of hydrogen chloride. An acid of this strength cannot leave a higher boiling residue, for it is itself the highest boiling mixture; it must, therefore, distil over *unchanged*, and this has been shown by experiment to be the case.

Conversely, if one starts with a stronger acid than 20%, a still stronger acid must distil over, for the weaker acid has the higher boiling point, and therefore remains behind. But this separation, also, cannot be carried on indefinitely, for when the content of the solution reaches 20%, no acid of higher boiling point can be formed, because there is no such, and the liquid must distil over unchanged.

We may therefore start with an acid of any concentration; on distillation, there ultimately always remains behind an acid of 20%, and a distillate consisting of a more dilute or more concentrated acid will be obtained according as one started with an acid containing less or more than 20% of hydrogen chloride.

* The error has often been made of regarding this constant boiling acid as a definite chemical compound. It is not one, for the composition of the constant boiling acid is dependent on the pressure under which the distillation is carried out. Under 2·3 atm., the mixture contains 18%, under 0·066 atm., 23%, of acid.

* On the contrary, on the basis of what has been said above, we may state the general theorem that every solution, the boiling point of which is higher than that of the neighbouring solutions on either side of it, will distil with constant composition. By quite similar reasoning it is easy to convince oneself that solutions, also, the boiling point of which is *lower* than that of the neighbouring solutions on either side, cannot be separated by distillation. In this case, however, the solution of unchanging composition appears not in the residue but in the distillate.

* Finally, the relations which have been described for hydrochloric acid give the explanation of a phenomenon which appears strikingly in the case of hydrogen chloride *gas*, and which is also noticeable in the case of concentrated hydrochloric acid, viz., the *fuming* of this substance in air. It is known that hot water fumes or forms a mist in the air, because, as a result of its higher temperature, it gives off more water vapour than can remain in the gaseous state at the temperature of the air. Water, however, of the temperature of the air can never form a mist, for it cannot possibly give off more vapour than can be contained in the vapour form in the air. Concentrated hydrochloric acid, however, fumes even without being warmed.

* The reason of this is that the evaporating hydrogen chloride encounters water vapour in the air, with which it forms a liquid the vapour pressure of which is much smaller than that of the concentrated acid. This solution must, therefore, be precipitated in the orm of a mist. Dilute acid does not fume, for the reason that its vapours cannot form a less volatile solution with the water vapour in he air, since they contain more water than the difficultly volatile 20% cid. On the other hand, the concentrated acid fumes only in moist ir; if acid, however concentrated, be placed in a bottle the interior f which is dried with sulphuric acid, no trace of fumes or mist is een.

* From these considerations we may conclude that every substance hich can form with water a solution (or compound) of considerably igher boiling point, must fume in moist air, whereas this cannot appen with substances which do not have that property. We shall

later frequently have an opportunity of applying and confirming this theorem.

Properties of Acids.—Hydrochloric acid, or the aqueous solution of hydrogen chloride, is a strong acid. In the name *acid* there is summed up a whole series of properties possessed in common by substances of different composition. Of these properties the longest known is the acid taste, which, as we know, is possessed by very different substances. A second property shown by all substances with acid taste, is the power of reddening the colouring-matter litmus (p. 150). A third common property is that of evolving hydrogen when brought into contact with certain metals, such as zinc or magnesium.

This last is, for us, the most important property of all. One can test whether it is a property of all acid substances by bringing acid liquids of all kinds, such as vinegar, acid fruit-juices, dilute hydrochloric acid or sulphuric acid, a solution of citric acid, etc., in contact with magnesium powder. In all cases, a more or less vigorous evolution of gas takes place, and on testing the gas, it is found to be hydrogen.

If we introduce the name acid for the substances possessing these properties, we can say that all acids contain hydrogen, which they evolve under the action of magnesium. The objection might be raised, that the hydrogen comes from the water in which all the acids were dissolved; with regard to hydrochloric acid, however, we already know that it contains hydrogen, and the same has been proved by chemical analysis with regard to the others. On the other hand, water does not appreciably act on magnesium at room temperature.

The properties we have just described are not possessed by all hydrogen compounds; they are wanting in the case of water, and also in the case of spirit of wine, petroleum, stearin, etc. It is easy to satisfy oneself that these substances contain hydrogen, by setting them on fire and holding over the flame a clean, dry glass; it is immediately covered with a dew of water drops. The hydrogen of the acids, therefore, must also be in the special condition mentioned on p. 181, by reason of which it acquires properties belonging only to the acids. These special relations we shall immediately explain.

Acids and Bases.—The properties which we have employed fo the identification of acids disappear when caustic soda (p. 150) i added to the acid liquids. This is seen most clearly in the case of th colour change with litmus. Dilute hydrochloric acid is coloured re by a drop of litmus solution. If a solution of caustic soda is now gradually added to this, the colour at first remains unchanged, the blue patches, which disappear on stirring, are seen in the liquid when the caustic soda drops, and finally, the whole liquid suddenly become blue. By working carefully, it is easy to recognise that the blu colour is produced by a single drop of the caustic soda solution.

At the same time, all the other properties of the acids have di appeared. The liquid no longer tastes acid and does not evolve hydrogen with magnesium powder. The same experiments can be performed with all the other acids.

A chemical reaction must therefore have taken place by the interaction of hydrochloric acid and caustic soda, the product of which is obtained by evaporating the liquid. A residue is obtained which, in all its properties, proves to be *common salt.*

Now, we know that common salt consists of chlorine and sodium (p. 172). If caustic soda and hydrochloric acid yield common salt, the other substances contained in them must have been converted into something else. These other substances are hydrogen from the hydrochloric acid, and oxygen plus hydrogen from the caustic soda. That makes up, however, the composition of water, and water is, in fact, the second product formed by the action of hydrochloric acid on caustic soda.

The relations are seen more clearly when the reaction is expressed in formulæ:—

$$NaOH + HCl = NaCl + H_2O.$$

The formation of water can likewise be proved by experiment. If dry hydrogen chloride gas is passed over some pieces of caustic soda, water vapour is formed with great evolution of heat, and can be condensed; after sufficiently long action, common salt remains as the residue.

There are many other substances which, like caustic soda, neutralise the properties of acids, giving rise to new substances accompanied by the formation of water. So far as they are soluble in water, they can be easily identified by the fact that they restore the blue colour to litmus, which has been made red by acids, and withdraw from the acids the property of evolving hydrogen with magnesium or other metals. They are the same substances as we previously (p. 151) got to know as being compounds of metals with hydroxyl, and which we called bases.

* The name base (foundation) is due to the fact that these substances represent the non-volatile constituent of salts, whereas most of the acids can be more or less easily expelled by heating. That portion which is more stable to heat was formerly regarded as the more important and was called the foundation or base.

Combining Proportions between Acids and Bases.—The process which takes place between bases and acids and which gives rise to the formation of a salt along with water, presupposes a perfectly definite ratio between the amounts of each. If we add a base to an acid, as much of the hydrogen will disappear as is necessary for the formation of water with the hydroxyl, viz., 1·01 gm. hydrogen to 17·01 gm. hydroxyl. So long as hydrogen is in excess, the liquid will exhibit an acid reaction, for this is not interfered with by the presence of the other substances. By continued addition of the base, a point will at last be reached when all the hydrogen has disappeared, and there is no excess of the base. Such a liquid will therefore exhibit the reactions neither of acids nor of bases; it will, for example, colour litmus neither blue nor red, but will leave its purple colour unchanged. Such a liquid is called *neutral.* This property is possessed by water and by the solutions of most of the salts. For example, common salt forms neutral solutions.

* Use can be made of these phenomena for many purposes. If it is a question of forming salts from acids and bases, litmus is used, best applied on paper, to determine if the components have been employed in the proper proportions; so long as blue litmus paper is coloured red, there is too little base; if red is coloured blue, there is too little acid.

* Litmus paper can also be used to show whether a salt is free from contamination with acid or base.

Reciprocal Estimation of Acids and Bases.—The most important application of these phenomena, however, is to the determination of the quantity or the concentration of acids and bases. If the same solution of caustic soda be always used, the amount of it required to neutralise different solutions of an acid will be proportional to the quantities of the acid.

The method of determination based on this is carried out as follows. The solution of caustic soda is contained in a tube of 1 to 2 cm. diameter, graduated by means of etched lines into cubic centimetres and fractions of these, and closed at the lower end by a tap. For most purposes a piece of rubber tubing can be used, which is pressed together by a brass pinch-cock; further, for the sake of the better regulation of the outflow a narrow glass tube, drawn out to a point, is inserted in the lower end. This apparatus is called a *burette* (Fig. 66).

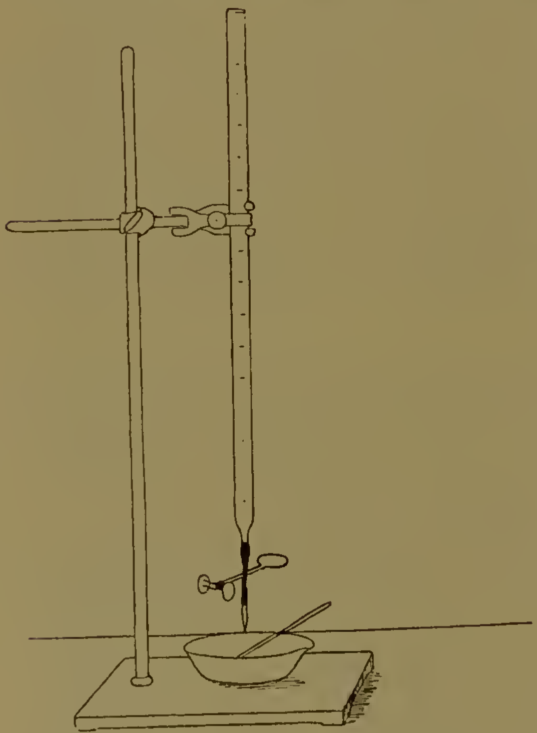
FIG. 66.

To determine the amount of acid in any given sample, *e.g.* of dilute hydrochloric acid, a drop of litmus solution is added; the burette is filled to the zero mark of the graduation with caustic soda solution, care being taken that no air bubbles are present in the tap and the outflow jet. The caustic soda is then allowed to flow into the acid until the red colour of this suddenly changes to blue. The approach of this point can be seen, since, shortly before it is reached, blue patches, which at first disappear on stirring, are formed where the caustic soda flows into the acid. The caustic soda is then added drop by drop, and the amount by which the blue coloration is produced can be obtained to within one drop. The amount of soda solution used can be read on the graduation of the burette, and from that the amount of acid can be calculated.

For this purpose the strength of the caustic soda solution must be known. As a rule, it is prepared so as to contain one combining weight, equal to 40·06 gm. of caustic soda, in one litre of solution. Such a solution is called *normal.* Exactly a litre of this solution is required to neutralise as much acid as contains 1·01 gm. hydrogen; for example, 36·46 gm. hydrogen chloride. If n cc. of the soda solution have been used, there must have been $\frac{n \times 36{\cdot}46}{1000}$ gm. hydrogen chloride present.

As a rule, it is not a matter of determining the absolute amount of acid, but the concentration of given solutions. To ascertain this, the acid contained in a definite amount of the solution has to be determined. This amount can be weighed out, but it is more convenient to measure it volumetrically. For this purpose, apparatus called *pipettes* are used (Fig. 67). They consist of narrow glass tubes, widened in the middle, and are made of such a size as to contain, up to a mark on the neck, a round number of cubic centimetres. To fill them, the liquid is sucked up past the mark; they are then closed by the forefinger and the liquid is allowed to run out exactly to the mark. Their contents are then emptied into the vessel in which the determination is to be made.

By the operation of neutralisation from a burette, or "titration," the amount of acid in the measured volume is ascertained, and from that it is easy to calculate the amount contained in unit volume, that is, the concentration. If, for example, we have measured off s cc. of acid with the pipette and have used n cc. of normal soda solution, the concentration is equal to n/s combining weights in a litre, or $n/1000s$ in a cubic centimetre. If M is the combining weight, $Mn/1000s$ is the amount of the substance in grams in a cubic centimetre.

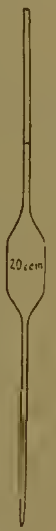

FIG. 67.

Volumetric Analysis.—This method of chemical measurement by means of liquids of known content, is called *volumetric analysis,* and the operation, *titration.* The method is not limited to the reciprocal determination of acids and bases; on the contrary, there are a number of other reactions which take place in aqueous solution accompanied by change of colour or other well-marked phenomena. On all such reactions methods of volumetric analysis can be based.

Solutions which in one litre contain one combining weight of the active substance in grams, are called *normal*.[1] If they contain only a tenth of this amount, they are called deci-normal ($n/10$), and so on. To prepare the solutions, the requisite quantities of the substances are weighed out and introduced into flasks of the desired capacity. This volume is exactly marked off by a ring on the neck of the flask (Fig. 68). Such vessels are called *measuring flasks*.

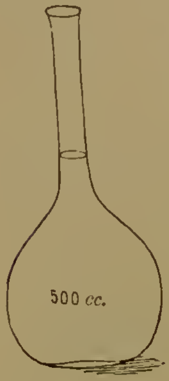

FIG. 68.

Lastly, *measuring cylinders* (Fig. 69) are used in volumetric analysis where comparatively large quantities of liquid have to be measured, the volume of which is not given in round numbers. They consist of cylinders set on a foot and furnished with etched graduation marks.

Ions.—It has already been several times pointed out that the hydrogen of acids behaves in an essentially different manner from the hydrogen of other compounds. It always gives the same reactions, independently of what the other components of the acids may be; for example, it is always displaceable by magnesium and other metals, and to it the common property of acids, that of reddening litmus, is due.

In the same way, the hydroxyl of bases always shows concordant properties. It is the cause of the reddened litmus being changed to blue, and on it depends the formation of new compounds, salts, with the simultaneous production of water, under the action of acids. These properties belong only to the hydroxyl of bases, and are not shown by other hydroxyl compounds which are known in large numbers.

A similar independence of the chemical properties of the compounds possessing them, is shown in the case of the salts. The following example will make this clear.

If a small quantity of a soluble *silver* salt, *e.g.* silver nitrate or lunar caustic (p. 57), is added to a dilute solution of hydrochloric acid, a white precipitate is immediately produced which, on shaking, becomes flocculent and looks like curdled milk, and which has the property of becoming grey when exposed to light.

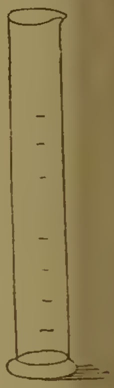

FIG. 69.

If, now, different salts are prepared from hydrochloric acid, either by decomposing the acid with metals or saturating it with bases, all these salts have the same property; they all yield the precipitate with silver salts, and the metal with which the hydrochloric acid has formed the salt is without influence on the production and nature of the precipitate.

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[1] In England it is customary to define a normal solution as one which contains in 1 litre the *hydrogen equivalent* of the active agent weighed in grams.—Tr.

Such a behaviour is by no means universal. In water and hydrogen peroxide we have got to know compounds which contain hydrogen or hydroxyl and still do not show the properties of acids or bases. Also, there are numerous chlorine compounds which give no precipitate with silver salts.

The survey of the chemical relations is, therefore, greatly facilitated by collecting into one special class the compounds which show these common reactions. It is called the class of the *salts* in the wider sense, acids and bases being included.

Salts are, therefore, characterised by the fact that in solution their components give individual reactions which are in each case independent of the other component present in the salt. And this relation is a reciprocal one; the second component also shows its own reactions, independent of the first.

Thus, hydrochloric acid exhibits, on the one hand, the properties of its component chlorine, by giving with silver solutions the precipitate described above. On the other hand, it exhibits the properties of its component hydrogen, by evolving hydrogen with magnesium. The former property it possesses in common with all salt-like compounds of chlorine; the second, with all salt-like compounds of hydrogen, *i.e.* with the acids.

These components of the salts which react independently of one another, are called *ions.* The name has been borrowed from their electrical properties, which will presently be discussed. In the acids, therefore, hydrogen is present as hydrion; in the salt-like chlorides, the chlorine is present as chloridion. The reddening of the litmus is a property belonging to hydrion; the precipitation of the silver salts, one belonging to chloridion.

The ions are therefore distinguished from the ordinary components of chemical compounds by the fact that they always have the same properties independently of the other ion along with which they occur. No less are they distinguished from the free elements or compounds of the same composition by the fact that they have, in the first place, other properties than these, and also that they can occur only in pairs. Thus hydrion of the acids is quite different from the ordinary gaseous hydrogen; for, whereas the former exhibits the reactions of acids which have been several times mentioned, none of these are shown by hydrogen gas, and whereas hydrogen gas is gaseous and dissolves only slightly in water, hydrion is known only in solution. Further, hydrion can be observed only in aqueous solutions of the acids in which the other components of the acids are simultaneously present which also have the properties of the ions. Thus, the other on of hydrochloric acid must be chloridion, since it contains no other omponent (p. 174). This chloridion, again, has properties which are dentical, no matter in what compounds it occurs (p. 188). In this ase also, chloridion is quite different from the element chlorine in the ordinary state. It has neither its colour, nor its smell, nor its bleaching properties; also, it exists not as a gas, but only in solution.

We have already got to know one case in which two substances have the same composition but nevertheless exhibit quite different properties, namely oxygen and ozone. This phenomenon was called allotropy (p. 80). In the same manner, we shall distinguish the gas hydrogen from hydrion as being two allotropic conditions of the same element; the same holds for chlorine and chloridion. Likewise, there are complex ions which have the same chemical composition as other substances which are not ions, but exhibit quite different properties. An example of this is hydroxyl and hydrogen peroxide. In the case of compound substances, this phenomenon is called *isomerism*, instead of allotropy; compound ions are, therefore, isomeric with the non-ions of the same composition.

* The distinction between the allotropic forms of the same substance, which was formerly (p. 80) recognised as essential, namely, that the *energy* content of each is different, obtains also for the ions and the non-ions of like composition. Between chlorine in the gaseous and the ionic state, there exists a considerable difference of energy in such a sense that the gas contains much more energy than the ion. In the case of hydrogen, the difference is only a small one. Conversely, there are cases where the ion contains more energy than the other form.

Salts are Electrolytes.—The chemical relations of the salts having led us to see in them a special class of compound substances distinguished by the independent behaviour of their components, the question arises whether there are other properties common to the salts connected with these special relations. The answer is in the affirmative; the salts exhibit many other common properties which we shall subsequently get to know individually. One of these properties is, however, so important and offers such far-reaching explanations that we shall discuss it just now. It is the behaviour of the salts towards the electric current.

As is known, substances behave differently towards the electric current; some are conductors of it, others are non-conductors. Metals are conductors; in sulphur we got to know a non-conductor (p. 7).

The conductors, again, are divided into two classes. To the first belong the metals. Such conductors experience, on the passage of the current, no other change than that they become warmer.

Conductors of the second class are chiefly aqueous solutions of certain substances. Simultaneously with the conduction of the current, they undergo a chemical change, their components being chemically separated and eliminated at the points of connection with the metallic conductor, or the "electrodes."

This phenomenon of decomposition by the electric current, is called *electrolysis*, and the substances which show it, the conductors of the second class, are called *electrolytes*. The metallic ends of the circuit in contact with the electrolytes, are called *electrodes*. We have several times, previously, made use of the phenomena of electrolysis for the purpose of separating and identifying the components of an electrolyte in a simple manner (pp. 137 and 176).

The exhaustive investigation of the substances which possess the property of electrolytes, has shown that they are ionic compounds or salts, and only these. *Salts are electrolytes, i.e.* the property of conducting the electric current, with decomposition, is inseparable from the presence of independently reacting components or ions.

Thus, water, for example, is not an electrolyte.[1] We can convince ourselves of this fact by means of the decomposition apparatus shown in Fig. 70. This consists of a beaker filled with the liquid to be investigated, to which the current from an electric cell (an accumulator) is led by two electrodes of platinum. This metal is chosen because it is not attacked by the substances which separate out at the electrodes; most of the other metals are not so resistant. To recognise the passage of the current any current indicator, *e.g.* an electric bell, can be used. A measurement of the current can at the same time be effected by using as indicator a current meter or ampere-meter, which must indicate hundredths of an ampere.

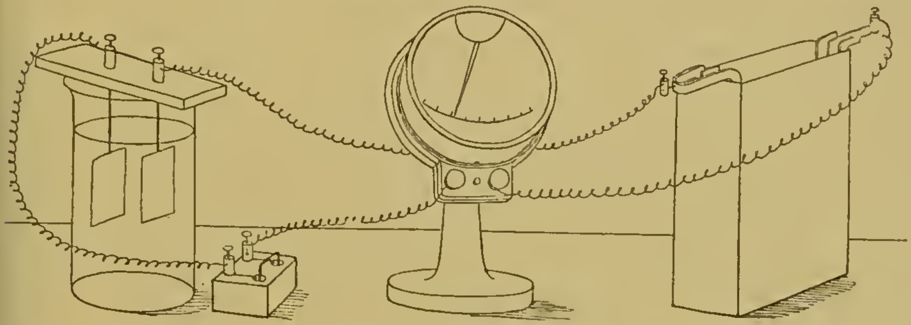

FIG. 70.

If the vessel is filled with pure water and the circuit closed, the instrument shows no deflection. On adding a little hydrochloric acid, austic soda, or common salt, to the liquid, a current forthwith passes, he measuring instrument shows a deflection, and gas is evolved at the lectrodes.

Anions and Cations.—The more exact investigation of the rocesses which take place in electrolytes under the influence of the urrent, has yielded the following results.

The hydrogen of the acids always separates at the so-called negative electrode, *i.e.* the electrode at which the positive current leaves the electrolyte to pass into the metallic conductor. At the same electrode, the metals of the salts appear. This is readily seen if a silver or copper salt be decomposed in the apparatus described; the former metal forms long, needle-shaped crystals, the latter covers the electrode with a red coating which exhibits the colour of pure copper.

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[1] Speaking strictly, water is certainly an electrolyte, but it possesses this property to n exceedingly small degree. A cube of water with a section of 1 sq. cm. conducts orse than a column of mercury a million kilometres in length, having a section of 1 sq. m. At a later stage we shall discuss the properties of water which depend on this small onductivity; we leave them out of account here, in order not to complicate the escription.

The ions which wander to the negative electrode and separate out there, are called *cations*,[1] and the electrode is called the *cathode*. Hydrogen is the cation of acids; the metals are the cations of the salts and bases.

At the second electrode chlorine appears in the decomposition of hydrochloric acid and of the salt-like metallic chlorides, and can be identified by its colour and its reactions. The ions which move in the opposite direction to the cations are called *anions*. Chlorine is therefore the anion of hydrochloric acid and of the metallic chlorides. The electrode at which the anions separate is called the *anode*.

For the sake of shortness, we have here, in the first place, designated that which separates at the electrodes by the name of the ions. It must, however, not be forgotten that the ions preserve their ionic nature only in the solutions. At the electrodes, the electric current passes on through the metallic conductors, while the ions are eliminated at these points. In this process the ions are converted at the electrodes into the allotropic or isomeric forms (p. 190), and this goes hand in hand with a change in their electrical relations, which we shall first of all consider.

The First Law of Faraday.—By a series of careful measurements, Faraday, in 1833, established the law that the amounts of the substances which separate at the electrodes are strictly proportional to the quantity of the electric current which was passed through the electrolyte. From this the idea arises that the passage of the electricity through the electrolyte is united with the simultaneous movement of the ions, so that no current at all can pass if it is not carried by the ions.

In accordance with the relation which we have just stated to exist between the direction of the current and the chemical nature of the substances which separate out, the cations (hydrogen and metals in the ionic state) are to be regarded as the carriers of quantities of *positive* electricity, whereas chlorine, as ion, transports negative electricity. At the electrodes, the current leaves the ions, being propagated in the metallic conductor without the simultaneous movement of substance.

We can therefore make the distinction between ions and the elements or compounds produced from them, clear to ourselves by regarding the ions as electrically charged substances, whereas the substances in the ordinary state are non-electrical. This view is a good representation of the actual relations, and it may be employed without entering more fully into the way in which the electrical charge on the ions is united with the substances. This new conception does not conflict with the criterion mentioned above (p. 190), that the ions differ from the non-ions of like composition in their *energy content*, for an electrically charged body has necessarily, in consequence of its charge, a different content of energy from an uncharged one.

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[1] The name is intended to express that these ions wander downwards in the direction of the electric current.

Electrical Units.—To enable the connection between the chemical and electrical phenomena to be clearly expressed, some of the fundamental laws of electricity must be here recalled.

By various means, such as galvanic cells, dynamos, thermopiles, etc., a process can be brought about in conductors of electricity which is called an *electric current*. By it, all kinds of work, both mechanical effects as well as chemical decompositions, can be performed at any point of the conductor, and heat or other forms of energy produced. The electric current, therefore, represents a special form of energy.

The current can be measured by applying the law of Faraday which has just been enunciated, according to which the *amount of electricity* passing through an electrolyte is proportional to the *amount of substance* which is at the same time decomposed. If, therefore, an electrolytic cell be introduced in the circuit, the quantity of gas evolved, for example, is a measure of the amount of electricity which has passed through. By *strength of current* there is understood the quantity of electricity which has passed, divided by the time required, or, the amount which passes in unit time. The strength of the current can therefore be measured by the amount of gas evolved in unit time.

The unit of quantity of electricity is called the *coulomb*; it has been determined in a manner which cannot be explained here. To reduce the coulomb to a measure with which we are familiar, we make use of the fact that for the evolution of 1·01 gm. hydrogen, 96,540 coulombs must pass through the electrolyte.

A current which in each second conveys one coulomb through the conductor, is called an *ampere*. In order, therefore, that a current of one ampere shall liberate 1·01 gm. hydrogen, it must flow for 96,540 seconds, or 26 hours and 49 minutes, through the electrolyte.

Very weak currents are measured in milliamperes or thousandths of an ampere.

A current is not determined by the number of amperes alone, for currents of the same number of amperes can produce very different effects, according to the nature of the conductor. The relations here are the same as in the case of a stream of water which can, with the same amount of water, perform various amounts of work, according to the pressure or the height of fall. The magnitude of the electric current corresponding to the pressure is called *potential*, and its unit is called the *volt*. For the present, however, we do not have to occupy ourselves with this magnitude.

Apparatus are made which depend on the magnetic action of the current, and on which the strength of the current can be read directly in amperes. For chemical purposes an instrument on which milliamperes can be read off, is the most suitable. For the measurement of stronger currents auxiliary apparatus (shunts) are given along with such instruments, which reduce the sensitiveness to a definite fraction, generally a tenth or a hundredth.

The Second Law of Faraday.—From the law that the ions of the electrolytes are united with definite amounts of electricity, some important conclusions can be drawn, which allow of a considerable extension of the electrochemical relations.

Hydrochloric acid solution is an electrically *neutral* body. If, then, the hydrion in it has a positive charge of the above large amount, there must also be negative electricity of exactly the same amount present. This is united with the chlorine, which thereby passes into chloridion. According to the law of combining weights, there are 35·46 gm. chlorine to 1·01 gm. hydrogen; consequently, one gram-ion or 35·46 gm. of chloridion, is united with 96,540 coulombs of negative electricity.

Similarly, the solutions of all salts are electrically neutral. If we consider, for example, such amounts of the different chlorides as contain 35·46 gm. chlorine, the amounts of the metals present along with it must also be united with 96,540 coulombs of positive electricity, independent of their nature. These amounts are equal to the combining weights of the respective metals, which are each united with one combining weight of chlorine; consequently we can state the universal conclusion:—

The amounts of the different ions united with the same quantities of electricity, are in the proportion of the combining weights of these ions.

In this form, the theorem holds, certainly, only when the combining weights are so chosen that they correspond to 1·01 gm. hydrogen or t 35·46 gm. chlorine. There are, however, metals which combine witl two, three, or more combining weights of chlorine; in their case the amount of electricity is a corresponding multiple, and they are calle polyvalent; likewise, there are polyvalent anions. We shall discus these relations at a later stage.

The theorem just enunciated was also discovered by Faraday, an is also called the law of Faraday. This law, therefore, contains tw laws which, indeed, are connected with one another but have respec to different things. Recapitulating all that has been said, we ma express it in the following form:—

In electrolytes, the electricity moves only with the simultaneous movemen of their components, the ions. The quantity of electricity transported is pr portional to the quantities of the ions and amounts to 96,540 coulombs, or multiple of this, for every gram-ion of any substance.

* The law of Faraday has a certain similarity to that of Ga

Lussac with respect to the volumes of gases in chemical combinations. Just as the amounts of gases present in equal volumes are proportional to the combining weights or to multiples of these, the amounts of the ions united with equal quantities of electricity are also proportional to the combining weights or to fractions of these.

* **Primary and Secondary Products of Electrolysis.**—If very dilute hydrochloric acid is subjected to electrolysis, hydrogen is obtained, as before, at the cathode; no chlorine, however, appears at the anode, but, in its stead, an equivalent amount of oxygen is evolved.

This is due to the fact that the water is decomposed by chlorine with formation of hydrogen chloride and oxygen, according to the equation $2H_2O + 2Cl_2 = 4HCl + O_2$ (p. 169). This process, it is true, takes place with measurable velocity, only in light; we may, however, assume here, as in similar cases, that the process takes place without light, only very slowly. It can, in fact, be accelerated by platinum and similar catalysers, even in the dark, to such an extent as to become measurable. The occurrence of oxygen in the electrolysis of dilute hydrochloric acid is, therefore, generally interpreted in such a way that it is assumed that chlorine is first formed, and that this then acts on the water, undergoing double decomposition with this to form oxygen and hydrochloric acid; the oxygen is accordingly called a *secondary* product of electrolysis.

Doubt, however, arises as to this view, because of the fact that it assumes hydrochloric acid to be *decomposed* by the current and to be *formed* again under the same conditions with the co-operation of the water present. Such an assumption can be avoided by means of suitable considerations; these, however, we shall not put forward here, but we shall formally retain the view just given, which has, in the first instance, no disadvantage and simplifies the discussion.

Such secondary products are often formed when the ions, after they are discharged, do not constitute substances which are stable under the existing circumstances.

Thus, copper and silver, as has been mentioned, are eliminated as metals from their salts; they are, therefore, primary products. If, however, sodium chloride is electrolysed, there is obtained (when concentrated solutions are used), on the one side, chlorine, but at the cathode there is obtained not sodium but hydrogen. This arises from the fact that sodium, which would be eliminated as "primary" product, cannot exist in contact with the aqueous solution, but must immediately pass into caustic soda with evolution of hydrogen (p. 83). One may, therefore, again assume that sodium is indeed eliminated, but that at the moment of its passing from the ionic into the metallic state it reacts with the water with formation of the secondary products. As a matter of fact, caustic soda is found at the cathode, for on adding red litmus solution to the liquid, it immediately becomes blue.

If a solution of caustic soda or sodium hydroxide be subjected to electrolysis, hydrogen, for the reasons just given, makes its appearance at the cathode. At the anode hydroxidion, OH, is discharged. This does not exist alone, but the doubled compound, O_2H_2 or hydrogen peroxide, is known. This substance, however, on account of its instability, is also not produced, or at least is so only in traces; on the contrary, the reaction $4OH = 2H_2O + O_2$ occurs, and free oxygen is evolved. This oxygen, therefore, is also to be regarded as a secondary product.

Faraday's law is necessarily fulfilled whether the products of the electrolysis are primary or secondary. For in the second case, the amounts of the secondary substances are always connected with those of the primary, by simple chemical equations, and the former must, therefore, necessarily be produced in amounts which are proportional and chemically equivalent to the primary.

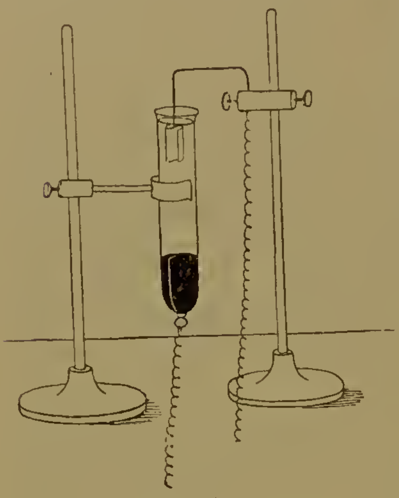
Fig. 71.

By slight changes in the conditions of the experiment, one may sometimes obtain the primary or the secondary products at will. For example, if, in the electrolysis of sodium hydroxide or sodium chloride, the platinum cathode be replaced by one of mercury (Fig. 71). no hydrogen is evolved but the sodium dissolves in the mercury. If, afterwards, the mercury containing the sodium be placed in pure water, the transformation $2Na + 2H_2O = 2NaOH + H_2$ slowly takes place; hydrogen is evolved and the liquid reacts alkaline.

Dissociation of Electrolytes.—An important fact, which sheds a further light on the difference between electrolytes and non-electrolytes, is the following. It has previously been explained that the molar weight of substances soluble in water, can be determined by the change which they produce in the freezing point of water, one mole of any substance dissolved in a litre of water causing a depression of 1·85°. If the quantity of hydrochloric acid which causes such a depression be determined, it is found that about 19 gm. are sufficient. Now, the smallest molar weight which can be assumed for hydrogen chloride is 36·46, the sum of the combining weights of chlorine and hydrogen; this molar weight, also, is obtained from the gaseous density of hydrogen chloride (p. 174). New relations, therefore, are met with here, which require a special interpretation.

This is obtained when we take into account the facts which have just been set forth concerning the independent behaviour of the ions. In the case of the other hydrogen compounds, as, for example, petroleum, spirit of wine, water, sugar, etc., no common property can be shown which could be attributed to the presence of hydrogen. The fact that they contain hydrogen appears only when the substances are destroyed and water has been formed from them by combustion. The behaviour of the substances containing hydrion is quite different; these are characterised just by the fact that they always exhibit the same properties, which are due to the hydrion. In these substances, therefore, the ionic hydrogen leads an *independent* existence, and can be recognised as exhibiting the properties of this.

We shall, accordingly, conclude that the solution of hydrochloric acid really contains two different substances, hydrion and chloridion, whereas the gaseous hydrogen chloride certainly contains only the compound and not the components. A solution of 36·46 gm. hydrogen chloride contains, therefore, not *one* mole of the compound, but two moles, one of each of the two kinds of ions. For that reason, it causes twice as great a depression of the freezing point. This observation, also, forces us to the conclusion that the ions are to be regarded as independent substances.

From the point of view, also, of the atomic hypothesis, a quite appropriate picture of these relations can be drawn. The investigations of the conductivity of electrolytes have shown that the movement of the electricity within these liquids takes place exactly as in metallic conductors, that it takes place, more especially, without expenditure of work so long as the substances are not eliminated at the electrodes and transformed. In other words, the electricity moves free in the electrolytes. Since, on the other hand, the electricity moves only simultaneously with the ions (cf. p. 192), there only remains the conclusion that the carriers of the electrical charges in the electrolytes, the ions, are also free.

An important conclusion can be immediately drawn from these general considerations. The deviations from the law of the depression of the freezing point and the electrical conductivities must run parallel to one another; where the one occurs, the other must also be present, and the two must be regularly dependent on one another. Experiment has shown that these conclusions are completely justified. The discovery of this important relation is due to the Swedish scientist Arrhenius (1887).

The phenomenon that certain substances (which shall henceforth be designated collectively as *salts*) break up, in aqueous solution, into independent portions, the ions, is denoted by the name of *electrolytic dissociation*. The name is formed in conformity with the term dissociation, which has long been in use to denote the partial decomposition of substances into simpler components. The epithet electrolytic refers to the phenomenon of electrical conductivity, which always accompanies this and which is present in all cases in which this phenomenon is found.

Electrolytic Solutions.—The properties of electrolytes just described can be observed only in *solutions*, and the question arises, whether the condition of solution has anything to do with the electrolytic dissociation. The answer is that such is the case to a very large extent. At the ordinary temperature, the property of electrolytic conductivity is exhibited, in any great degree, only by *dissolved* salts; pure substances are either non-conductors or exceedingly poor conductors. This holds for all three physical states, and more especially for liquids. At a comparatively high temperature, pure substances, *e.g.* the ordinary salts in the fused state, also begin to conduct.

Further, the property of electrolytic conduction belongs chiefly to aqueous solutions. Solutions in other liquids sometimes also exhibit electrolytic conduction, but this is, in general, much less than in aqueous solution, so that, in this respect, water occupies an exceptional position.

These relations are exhibited very clearly in the case of hydrogen chloride. Hydrogen chloride can be obtained in the pure state as a liquid (p. 179), which, however, exhibits no acid properties so long as no water is added to it. Metals do not evolve hydrogen from it, and in its behaviour it is rather indifferent. It is only when the hydrogen chloride is dissolved in water that the typical properties of the acids make their appearance; these properties are dependent on the formation of hydrion, which occurs only on dissolution in water.

Since most of the chemical reactions, more especially the *analytical* ones, which serve for the identification of different substances, are carried out in aqueous solution, a knowledge of the ionic condition of the salts is a matter of great importance. In the case of all compounds, therefore, we shall in future state whether they form ions, and which these are.

The *names* of the substances in the ionised condition are formed according to the following rules. The names of the cations are obtained by adding the termination -ion to the stem of the names of the corresponding metals, the Latin names for the latter, where such exist, being employed. Hydrogen in the ionised condition, however, is called hydrion. Where a substance forms several ions differing from one another in valency, the names of such ions are distinguished by prefixing a Greek numeral indicating the valency. In the case of the anions, the names are formed from those of the salts as follows. If the name of the salt ends in -ate, the name of the corresponding anion is obtained by replacing the termination -ate by -anion; except the anion of the carbonates, which is called carbanion. The names of the anions of salts ending in -ite are formed by replacing -ite by -osion, and of salts ending in -ide by converting this termination into -idion. The ion OH′ is called hydroxidion.

* The above names are the names of *substances*, and do not express any *molecular* conceptions.

Further, we shall sometimes find it necessary to distinguish the substances in the condition of ions from the others. For this purpose, the cations will be designated by a point, the anions by a dash. $H^{\cdot}$ represents, therefore, hydrion; Cl', chloridion. On account of the necessity that chemically equivalent amounts of cations and anions must be present in solutions (p. 194), every complete chemical equation must, when ions occur in it, contain equivalent amounts of cations and anions on the same side of the sign of equality.

Thus, for example, the process of the formation of sodium chloride from hydrochloric acid and caustic soda, will have to be represented by the following equation, if it is desired to represent the processes by the ions:—

$$\overbrace{H^{\cdot} + Cl'} + \overbrace{Na^{\cdot} + OH'} = \overbrace{Na^{\cdot} + Cl'} + H_2O.$$

This equation shows that the ions chloridion and sodion remain unchanged in the process, as their reactions, indeed, also persist in the solution of common salt produced. For this gives, on the one hand, the precipitate with silver salts which is characteristic of chloridion, and, on the other hand, when electrolysed with a mercury cathode, it yields a solution of sodium in mercury, just as caustic soda also does (p. 196).

The ions hydroxidion and hydrion, however, are used up, because they have combined to form undissociated water (p. 191). For this reason the reaction both of hydrion and of hydroxidion have disappeared, for the liquid no longer reacts acid, nor can the basic properties of caustic soda be any longer detected.

Thermochemical Relations of Hydrogen Chloride.—Since chlorine burns in hydrogen, the heat developed in the combustion can be directly measured; the following equation is thus obtained:—

$$Cl_2 + H_2 = 2HCl + 2 \times 92\ kj.$$

This number applies to the formation of gaseous hydrogen chloride. If this is dissolved in water, a further very considerable quantity of heat is developed. The necessity is here felt of distinguishing the dissolved hydrogen chloride from the gaseous, since these two forms possess, in conformity with the difference of their properties, very different energy.

Where we are dealing with aqueous solutions, it has become customary to designate the condition of *solution* of substances by the addition of aq. (aqua). Now, certainly, the development of heat on dissolving hydrogen chloride varies, according as the solution produced is more or less concentrated. This is easily seen from the fact that on diluting a concentrated solution of hydrochloric acid, a fairly large quantity of heat is developed. If, however, the dilution is carried further, this heat becomes less and less, and there is ultimately a final condition reached when a measurable quantity of heat is no longer developed. It is to this condition that the symbol aq. refers.

If hydrogen chloride is dissolved in a large quantity of water, 72 *kj* are developed, and we have the equation

$$HCl + aq. = HCl\ aq. + 72\ kj.$$

On adding this equation (multiplied by 2) to the preceding one, there follows

$$H_2 + Cl_2 + aq. = 2HCl\ aq. + 2 \times 164\ kj,$$

which gives the heat of formation of the dissolved hydrochloric acid from its elements.

Thermochemistry of the Salts.—If a strong acid, *e.g.* hydrochloric acid, is neutralised with a strong base, *e.g.* caustic soda, a quantity of heat equal to 57 *kj* is developed. The quantity of heat is found to be identical, no matter what acid or base is used, it being assumed that both are "strong," and that both are in the condition of dilute aqueous solution.

The reason of this law becomes at once apparent if we recall the fact that the formation of a salt from its acid and base in dilute aqueous solution, consists in the hydrion and the hydroxidion combining to form water, while the two other ions remain unchanged side by side (p. 198). The heat development of 57 *kj* is nothing else than the heat of formation of water from hydrion and hydroxidion. Since in the formation of any and all salts from strong (*i.e.* nearly completely dissociated) acids and bases, the same process of the formation of water always takes place, the corresponding heat development must also have the same value.

At the same time it follows that deviations are, in general, to be expected, if any of the suppositions made are not fulfilled, *i.e.* if acid, base, or salt is slightly dissociated. To the heat of formation of water, 57 *kj*, there must then be added the quantity of heat which is developed or absorbed in the decomposition of the acid or base into its ions or in the formation of the undissociated portion of the salt, and the observed heat of neutralisation is the sum of the corresponding magnitudes. We shall have an opportunity later of mentioning such cases.

Further, it was mentioned on p. 190. that the elementary ions have different quantities of energy from the free elements. It may be asked if it is possible to measure this difference.

A method, which cannot be described here, has, indeed, been found for this purpose; but since no other method of attaining the same object could be found, it has hitherto not been possible to test its result. It led to the conclusion that the transformation of hydrogen gas into dissolved hydrion causes no appreciable change of energy. We have, therefore, the following thermochemical equation:—

$$H_2 + aq. = 2H^{\cdot}\ aq. + 0\ kj.$$

If this basis be assumed, the heats of formation of all other ions can be determined.

For example, it was found (p. 200) that a dilute aqueous solution of hydrochloric acid is produced from its elements and water with a heat development equal to 164 *kj*. Since this solution contains chlorine and hydrogen in the form of ions, we should, taking this into account, write the equation :—

$$\begin{aligned} Cl_2 + H_2 + aq. &= 2(Cl' + H^{\cdot})\ aq. + 2 \times 164\ kj \\ &= 2Cl'\ aq. + 2H^{\cdot}\ aq. + 2 \times 164\ kj. \end{aligned}$$

Subtracting from this the equation $H_2 + aq. = 2H^{\cdot}\ aq.$, there follows

$$Cl_2 + aq. = 2Cl'\ aq. + 2 \times 164\ kj.$$

In other words, the heat of formation of dilute hydrochloric acid is equal to the heat of formation of chloridion, since no heat effect is produced in the formation of hydrion.

This conclusion can be at once generalised. Since, as regards the hydrion, the same relations are found in the case of all acids so far as they are electrolytically dissociated, the rule obtains for all acids that the heat of formation of their dilute aqueous solutions is equal to the heat of formation of their anion.

When sodium is dissolved in hydrochloric acid, the hydrogen of the acid escapes and sodium chloride is produced. The development of heat which thereby occurs, is very considerable. This has been determined, indirectly, and been found equal to 239 *kj*. This corresponds, therefore, to the equation

$$2Na + 2HCl\ aq. = H_2 + 2NaCl\ aq. + 2 \times 239\ kj.$$

If we again write the ions, the equation runs :—

$$2Na + 2H^{\cdot}\ aq. + 2Cl'\ aq. = H_2 + 2Na^{\cdot}\ aq. + 2Cl'\ aq. + 2 \times 239\ kj.$$

If we again subtract the equation $H_2 + aq. = 2H^{\cdot}\ aq.$ from this and omit, on each side, the common member Cl' aq., we obtain

$$Na + aq. = Na^{\cdot}\ aq. + 239\ kj.$$

That is to say, the conversion of metallic sodium into sodion is accompanied by a development of heat of 239 *kj*. This is the same amount of heat as was developed in the action of sodium on hydrochloric acid, for the simultaneous conversion of hydrion into gaseous hydrogen gives no heat effect.

This theorem, also, can be extended generally. It holds for every other dissociated acid and every other metal. We can, therefore, enunciate the general law :—

If a metal acts on an acid with the formation of a salt and generation *of hydrogen, the amount of heat which is developed depends only on the nature of the metal, and is independent of the acid.* This heat is equal to the heat of transformation of the metal into its cation.

The first part of this law is an experimental fact, and was known long before it was deduced on the basis of the theory of electrolytic dissociation.

Should any of the substances with which we are dealing be undissociated or only slightly dissociated, deviations from the simple law occur; the cause of these is the same as in the case of the deviations from the constant heat of neutralisation, discussed on p. 200.

The transformation, therefore, both of chlorine and of sodium, from the ordinary to the ionic condition, is accompanied by a very considerable development of heat. Although the difference of the total energy of the two conditions, of which the heat development is an expression, is not a direct measure of the tendency of the elements to pass into the ionic condition, still the one moves to some extent parallel to the other, and from the large values of the heat development we can infer a large value for the tendency to transformation. In fact, it has been repeatedly mentioned that both elements possess a very considerable chemical reactivity. On examining the nature of these reactions of chlorine and sodium more closely, it is found that in the majority of the cases *salts* are formed, that is to say, we have before us a manifestation of the tendency of chlorine and sodium to exchange the ordinary for the ionic condition.[1]

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[1] Even in the *solid* salts, which are not electrolytically dissociated, the components are much nearer to the condition of the ions than to that of the free elements. This is seen from the fact that the passage of the solid salts into the ionic condition, on being dissolved in water, gives rise, in general, to only inconsiderable heat effects, in most cases, indeed, to absorption of heat.

CHAPTER X

OXYGEN COMPOUNDS OF CHLORINE

Oxygen Compounds of Chlorine.—Whereas hydrogen can combine with chlorine only in one proportion, this latter element forms several compounds with oxygen. There is a still larger number of substances which contain hydrogen along with chlorine and oxygen.

All these compounds are distinguished from hydrogen chloride by a circumstance of essential importance. They bear the same relation to it as hydrogen peroxide does to water; hydrogen chloride is formed from its elements with loss of energy, and cannot, therefore, decompose spontaneously into them, but, for the production of the oxygen compounds of chlorine, energy must be communicated. Accordingly, these compounds exhibit the property of decomposing spontaneously, *i.e.* without the communication of energy, and this instability is so marked in the case of some of them that they decompose with explosion. The reason for this is in entire accordance with the relations set forth in the case of hydrogen peroxide (p. 159).

The way in which the energy necessary for the formation of such compounds must be communicated, may vary in different cases. The most frequent and, for general reasons, the most important way for us, s the *chemical*. If the possible processes are conducted in such a way that along with the desired substance, other substances are produced whose formation is accompanied by the liberation of large quantities of energy, this energy can be used for the purpose of producing the comparatively unstable compound. For the successful communication of this energy, however, it is not sufficient that any reaction whatever, which will yield energy, be allowed to take place along with the desired one; such a reaction would act merely as a corresponding elevation of the temperature, and it would have no effect, or only a harmful one. *On the contrary, it is an essential condition that the two reactions be dependent on one another, or be "coupled" with one another, so hat the one cannot take place without the other.* It can be seen from the hemical equation whether this condition is satisfied. If this can be eparated into two equations which are independent of one another, the chemical processes are not "coupled"; if such a separation cannot be made, the above condition is satisfied.

Thus, for example, it might be expected that the large development of energy which accompanies the formation of water from its elements, could cause the simultaneous formation of hydrogen peroxide from oxygen and hydrogen, the energy necessary for this latter reaction being yielded by the former by some such reaction as is expressed by the equation

$$3H_2 + 2O_2 = 2H_2O + H_2O_2.$$

This expectation is not confirmed by experience, a fact which is in harmony with the rule just given, for the equation can be resolved into the two equations

$$2H_2 + O_2 = 2H_2O \text{ and } H_2 + O_2 = H_2O_2.$$

The two processes are, therefore, not coupled or mutually conditioned.

Numerous examples of coupled processes will be given by the reactions which lead to the formation of the oxygen compounds of chlorine, and which will be given immediately.

Hypochlorous Acid.—It has been already mentioned (p. 168) that chlorine is absorbed by caustic soda solution. The product formed cannot consist entirely of sodium chloride, for this is formed from caustic soda and *hydrogen chloride*. As a matter of fact, sodium chloride is indeed formed, accompanied, however, by a new substance.

The solution produced has not the purely saline taste of common salt, but a caustic one. Like free chlorine, it has a bleaching action on vegetable colours, *e.g.* litmus; it acts as a powerful disinfectant and, on the addition of hydrochloric acid, it evolves chlorine, which can be identified by its colour and smell. Common salt, however, gives no detectible reaction with hydrochloric acid.

The above process takes place, according to the equation

$$2NaOH + Cl_2 = NaCl + NaOCl + H_2O.$$

There are formed, therefore, sodium chloride and another compound which contains oxygen.

If this compound, NaOCl, be prepared free from sodium chloride it is found that its aqueous solution is an electrolyte, but does not give the reactions of chloridion, for no precipitate is obtained with silver salts. The crude solution, which contains sodium chloride, of course gives this precipitate, but only in half the amount that corresponds t the chlorine present.

From this it follows that this second substance is, indeed, a salt, bu contains no chloridion. The chlorine must, therefore, be present i some other combination, and the most obvious possibility, and the on which agrees with actual fact, is that it forms an ion OCl′ with th oxygen, sodion being the other ion of the salt.

There must therefore be an acid HOCl, formed by the combination of hydrogen with the ion OCl′, which on neutralisation with caustic soda again yields the original salt, according to the equation $HOCl + NaOH = NaOCl + H_2O$. Such an acid can, indeed, be prepared. This acid has received the name of *hypochlorous acid*; its salts are called *hypochlorites* and the ion OCl′ *hypochlorosion*. The sodium salt already mentioned is called *sodium hypochlorite*.

Preparation of Acids from their Salts.—For this purpose a general method is used, which can be described in the following words: *To obtain the acid corresponding to a given salt, the salt is decomposed with another acid.*

That such a preparation is possible can be seen if we designate the desired acid by HA, where A is a simple or complex anion, and its salt by MA, where M represents some metal ion. Further, if HB is another acid, the following reaction is possible by the interaction of the two substances :—

$$MA + HB = HA + MB.$$

There would be obtained, therefore, if the reaction took place, the desired acid and the salt of the acid added. There remains then the further task of separating the two substances in order to obtain the acid in a pure state.

Applying this rule at once to the case before us, we should have to decompose the sodium salt NaOCl with hydrochloric acid. The desired acid, along with sodium chloride, would be obtained, according to the reaction

$$NaOCl + HCl = NaCl + HOCl,$$

and the two substances would then have to be separated.

It has been found, now, by experience that the reaction represented by the general scheme always occurs, but is never a complete one. In all cases only a portion of the substances present undergoes reaction, and another portion remains unchanged. In other words, in all these cases chemical *equilibria* are established (p. 100). For such equilibria it is necessary that the concentrations of the reacting substances shall be in a definite relation to one another, depending on the nature of the substances, on the temperature, and on several other circumstances.

If, now, one of the participating substances is removed, the equilibrium can no longer exist, but the reaction must take place by means of which the substance removed is again replaced. If the portion thus formed is also withdrawn, the same process goes on again, and in this way the reaction can be carried so far that the total possible amount of the product is ultimately formed.

On this fact is based the preparation of hypochlorous acid by the reaction described. If dilute hydrochloric acid is added to the sodium hypochlorite, part of the salt is converted into sodium chloride and hypochlorous acid, while another part remains undecomposed. On distilling the mixture, the hypochlorous acid, which is the most volatile of the four substances present, passes over, and the amount of it in the residue is diminished. For this reason fresh acid must be formed in the residue ; if this is also removed by distillation, all the acid which can be formed from the quantities of the substances present, must really be ultimately formed, and be found in the distillate. And this is, as a matter of fact, the case.

In carrying out the experiment it is necessary to proceed with care and to add less hydrochloric acid than corresponds to the equation. Also, it is necessary to employ dilute acid and to so add it that there can nowhere exist an excess of hydrochloric acid. In the present case this is necessary because of the fact that hydrochloric acid acts on the hypochlorous acid, as will be presently discussed. In other cases, where such action is not to be feared, these precautions are unnecessary.

Properties of Hypochlorous Acid.—The aqueous solution of hypochlorous acid, obtained in this manner, shows not only the general properties of acids but also some special properties, which in many cases mask the former. The solution is colourless but has a strong smell, similar to that of chlorine. It acts as a powerful bleaching agent towards organic colouring matter, and its action as a disinfectant and as a poison for small organisms, is almost equal to that of chlorine.

The great similarity shown by the solution of hypochlorous acid to an aqueous solution of chlorine, is due to the fact that the latter undergoes a partial transformation into hypochlorous acid and hydrochloric acid, according to the equation

$$Cl_2 + H_2O = HOCl + HCl.$$

This reaction, also, does not take place completely, but only partially and to an extent which is dependent on the concentration and the temperature. In the reverse manner, hydrochloric acid and hypochlorous acid act on one another with formation of chlorine and water.[1] This reaction, however, is also not a complete one, and, therefore, the rule which has just been given, that the reaction can be made to take place completely in the one or the other direction, by removing the corresponding reaction products, will hold also for it.

Decompositions of the Hypochlorites.—The most importan of the special properties of hypochlorous acid depend on the fac that it loses its oxygen with extreme readiness, thereby passing into hydrochloric acid. Similarly, the hypochlorites pass into chlorides, or hypochlorosion into chloridion. Expressed in equations, we have

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[1] This is the reason why the decomposition of sodium hypochlorite with hydrochlori acid must be carried out carefully so as to avoid having at any time an excess of the aci present at any point. If this care is not observed chlorine is formed, which, on distillation, passes over with the hypochlorous acid and renders it impure.

$$2HOCl = 2HCl + O_2,$$
$$2NaOCl = 2NaCl + O_2,$$
and
$$2OCl' = 2Cl' + O_2.$$

If, therefore, they are brought together with substances which can take up oxygen, these will unite with oxygen or be oxidised. For this reason, the hypochlorites are powerful oxidising agents, and in this respect are superior to hydrogen peroxide.

This readiness to part with oxygen is seen even in the case of the hypochlorites from the fact that they evolve gaseous oxygen. Under ordinary conditions, this process takes place so slowly that it is scarcely noticeable. Like all slow reactions, however, it can be made to take place much more quickly by means of accelerating agents, and can then be readily observed.

In this case, such catalytic agents are, more especially, the salts of *cobalt*, a metal belonging to the same class as iron (p. 54). On adding a small quantity of any cobalt salt to a solution of sodium hypochlorite obtained by passing chlorine into a solution of caustic soda, a black precipitate is produced which is an oxide of cobalt rich in oxygen, and gas is immediately evolved. This can readily be shown to be oxygen from its causing a glowing splinter to burst into flame.

The formation of the hypochlorite and its decomposition into chloride and oxygen, can be united into *one* process by adding some cobalt salt to a solution of caustic soda and passing in chlorine. The hypochlorite is then only temporarily formed, and forthwith decomposes into chloride and oxygen. The process then appears to take place in accordance with the equation

$$4NaOH + 2Cl_2 = 4NaCl + O_2 + 2H_2O.$$

In accordance with the general law for catalytic processes, we must in this case also say that the formation of oxygen is a process which takes place spontaneously, and can only be *accelerated* by the catalyser. In the formation of hypochlorite also, by passing chlorine into caustic soda the above process takes place at the same time, and a slight evolution of oxygen occurs. It might now be asked why hypochlorite is formed at all, and why the whole amount of the substances does not straightway pass into the most stable condition, chloride and oxygen, as represented in the last equation.

Law of Successive Reactions.—The answer to this question is again afforded by a general law, which states that *in all reactions the most stable state is not straightway reached, but the next less stable or that state which is the least stable of the possible states.* Starting from this, the more stable states are reached one after the other, and the process of transformation comes to a stop only when a state is finally attained which cannot further change and is, therefore, the most stable.

To understand this theorem aright it is necessary to have a clear idea of what the stability of a system depends on. Reference has already been made at an earlier stage to these relations when treating of oxidising agents (p. 154), and we shall here treat the question in a more general manner.

Free Energy.—Every process that takes place spontaneously, is characterised by the fact that by its progress work can in some way be gained. No such process can take place of itself, under the same conditions, in the reverse manner; to bring about this reversal, work must be again communicated. Thus, water flows of its own accord, valleywards, and can thereby perform work; but to bring it uphill, it must be carried or pumped up, and for that, work is always necessary.

The least stable conditions are, therefore, those which contain the most work, and the most stable are those from which as much work has been taken from the system as it will yield. The word "work" is here used in its most general meaning; it represents, therefore, some form of energy (p. 21).

From the preceding statement it might be concluded that the most stable conditions are those with the smallest, and the least stable those with the largest, amounts of energy. This would be the case if all the energy contained in a system could be transferred without more ado to another system or could be converted into work. That this cannot be done will be seen if it be attempted, for example, to utilise the pressure of the atmosphere to perform work. Although the air, under the ordinary pressure, could perform a very considerable amount of work if it were enclosed in a space in which a much lower pressure prevailed, it cannot be made to perform any work if its surroundings are under the same pressure.

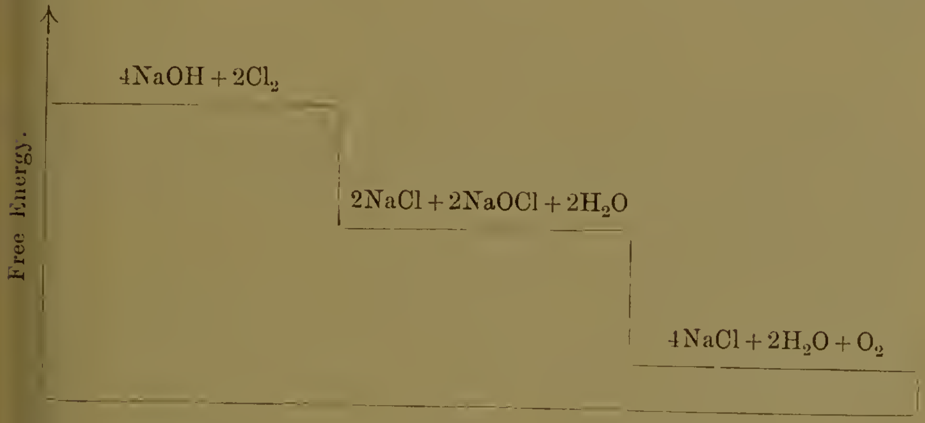
It is necessary, therefore, to distinguish between the energy which is transferable to other systems and that which does not possess this property. The former is called *free*, the latter *latent*. *The total energy of a system is, therefore, the sum of its free and its latent energy.* All processes which take place spontaneously do so only with diminution of the *free* energy; for, after all, we understand by a process nothing but the transference of energy from one system to another.

Having established these conceptions, we can, therefore, say that all chemical processes can take place only in such a way that the *free energy* decreases. The least stable form will, therefore, be that with the greatest free energy; the most stable, that with the least.

The *total energy* need not necessarily run parallel with the free energy, for it is quite possible that as the free energy decreases, the latent increases all the more, so that the total energy also increases. Such a system will fall in temperature during the process, since the necessary energy is drawn, almost without exception, from the heat contained in it. To this class belong, therefore, all processes which take place spontaneously with fall of temperature. Examples of this are not rare. A volatile liquid evaporates spontaneously with fall of temperature into a space which is free from its vapours; salts dissolve spontaneously in water with fall of temperature, and many chemical processes also take place spontaneously with fall of temperature. All these cases are examples of the fact that in spite of the decrease of the free energy in processes which take place spontaneously, the total energy can increase.

The question as to how the free energy is to be measured cannot be discussed here. It is sufficient to know that the fact that a reaction takes place spontaneously is a sign that the free energy of the system is thereby diminished.

If we apply what has here been said to the case we were just considering, the system chlorine plus caustic soda will be designated as the form with the greatest free energy. The system produced from this, sodium chloride plus sodium hypochlorite, has less free energy, and sodium chloride plus oxygen has the smallest amount of free energy. The following figure gives a picture of the relations, the values of the free energy being represented by the perpendicular heights:—



From the appearance of the figure it will be seen why it is that, tarting from the highest step, the lowest is not immediately reached, ut that a halt is first made at the middle one. This furnishes an nswer to the question asked above (p. 207).

Chlorine Monoxide.—Hypochlorous acid is not known in the ure, *i.e.* the anhydrous, state. On attempting to prepare it, the lements of water leave the acid, and a compound of chlorine and xygen remains behind. This compound is no longer an acid, since it ontains no hydrogen.

This process takes place in accordance with the equation

$$2HOCl = H_2O + Cl_2O.$$

The new substance is called chlorine monoxide, since it contains *one* combining weight of oxygen. Since it is obtained from hypochlorous acid by loss of water, it is also called hypochlorous anhydride. This nomenclature is employed fairly generally; various substances which are formed from other substances by the loss of the elements of water, are called *anhydrides* of these substances.

* This name was introduced on the supposition that in the original substances not merely the elements of water are contained but also ready formed water, and this conjecture arose because some substances give off water with exceeding readiness and rapidity. But a deeper knowledge of the facts has shown that there exists a continuous transition from those which readily give off water to those from which water can be obtained only by especially powerful reactions. It is, therefore, more scientific to in no case assume the presence of preformed water, especially as no definite meaning can be attached to such a supposition.

Chlorine monoxide is obtained most readily by carrying out the reaction leading to the formation of a salt of hypochlorous acid (p. 204), with an oxide from which the salt is not formed. For this purpose oxide of mercury is the best. When a current of dry chlorine is passed over mercuric oxide,[1] the following reaction takes place:—

$$HgO + 2Cl_2 = HgCl_2 + Cl_2O.$$

In this equation Hg is the symbol for mercury; its oxide is composed of equal combining weights of mercury and oxygen. The chlorine compound of mercury, or mercuric chloride, remains behind as a solid substance, and the chlorine monoxide, which is gaseous at room temperature, escapes and can be collected.

Chlorine monoxide is a yellow-brown gas with a strong, unpleasant smell, which can be condensed to a liquid at 5°. It dissolves in water, passing slowly into hypochlorous acid. In the gaseous and still more in the liquid state, it is very unstable and readily decomposes with explosion, forming oxygen and chlorine. These explosive properties find an explanation in the fact that heat is liberated by the decomposition (p. 159). The gas also decomposes into its elements under the influence of light, but generally without explosion.

Chloric Acid—Formation of Sodium Chlorate.—The steps in the transformation of chlorine and caustic soda described on p. 209 are not the only possible ones, for there are still two others which lie between the middle and the lowest. The solution of $NaCl + NaOCl$, which is obtained by passing chlorine into a solution of caustic soda, undergoes a change in its properties on being kept some time. This change takes place most quickly in the heat and when a slight excess of chlorine is present in the solution. Its bleaching power and its smell gradually disappear, and after some time it contains no more hypochlorite, for it evolves no chlorine on being treated with dilute hydrochloric acid in the cold.

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[1] In order that the reaction may take place satisfactorily, the mercuric oxide required for this experiment must be of a special nature. If too finely divided, the reaction goes too quickly and an explosion may occur; if it is too coarse, the reaction will be too slow and the gas will be contaminated with chlorine. A suitable oxide is obtained by gently heating the oxide prepared by precipitating mercuric chloride with caustic soda in aqueous solution.

If the solution is now evaporated, two salts are obtained, sodium chloride and another salt which, like sodium hypochlorite, also contains oxygen. It is shown, however, by analysis, to have a composition which is expressed by the formula $NaClO_3$, and is called *sodium chlorate*. The reactions which take place are, therefore, represented by the equations

$$2NaOH + Cl_2 = NaCl + NaOCl + H_2O,$$
$$3NaOCl = 2NaCl + NaClO_3,$$

or, omitting the intermediate stage,

$$6NaOH + 3Cl_2 = 5NaCl + NaClO_3 + 3H_2O.$$

Since sodium chlorate is a very soluble salt, and can be separated only with difficulty from the simultaneously formed sodium chloride, t is better to prepare the corresponding potassium salt by passing chlorine into a solution of potassium hydroxide. Since potassium in all its chemical relations exhibits an exceedingly great similarity to odium, the reactions which take place are of exactly the same kind as hose described, and need not be again explained. Potassium chlorate along with potassium chloride, is obtained as the product of the reaction; and since the former salt is much less soluble than the latter in he cold, it separates out on allowing the solution, obtained by the ction of chlorine on potassium hydroxide, to cool.

The salt thus obtained is already well known; it is the salt used or the preparation of oxygen in the laboratory (p. 62). The otassium chloride formed at the same time is a salt very similar to odium chloride.

From what was previously stated, it is known that potassium hlorate, on being heated, decomposes into oxygen and potassium hloride, the same behaviour being likewise shown by sodium chlorate. he decomposition takes place according to the equation

$$2KClO_3 = 2KCl + 3O_2,$$

here K is the symbol for potassium.

As can be seen, this is the last step in the action of chlorine on ydroxides, and to the three steps given on p. 209 there must be added fourth, between the hypochlorite and the lowest. We shall soon e that even a fifth step must be inserted.

In conformity with the smaller fall between the chlorate and the oxygen steps, the last transformation does not proceed so readily and rapidly as that of chlorine into hypochlorite, and of the latter into chlorate. At ordinary temperatures, the chlorates are practically quite stable, and only at comparatively high temperatures does the reaction become so rapid that it can be observed. That the reaction can be accelerated through the influence of catalytic agents, has already been mentioned (p. 62); besides the substance then mentioned, pyrolusite, oxide of iron is a very effective accelerator of the decomposition.

Preparation of Chloric Acid.—Chloric acid cannot be very easily obtained from potassium or sodium chlorate. The aqueous solution of the salt, it is true, undergoes partial decomposition by other acids, in accordance with the general rule (p. 205); but as the chloric acid cannot be distilled, the separation cannot be carried out in the same way as in the case of hypochlorous acid. Recourse has, therefore, to be had to another method.

If we consider the equation

$$MA + HB = MB + HA$$

given on p. 205, we see that the desired acid can be prepared not only by removing it from the sphere of the reaction, but it will be obtained alone by completely removing the salt MB. As a rule, certainly, the salts are not volatile, so that the method of distillation used for removing the acids cannot be employed. On the other hand, however, many salts are insoluble, and by their precipitation the reaction is made as complete as by the removal of the acids.

To carry this idea into practice, the components M and B have only to be chosen so that they together give an insoluble salt; that is to say, a salt of the desired acid has to be prepared which yields an insoluble salt with another acid, and with this acid the salt has to be decomposed.

Now, we already know a metal which gives an insoluble salt with hydrochloric acid, viz. silver. Silver chloride is so highly insolubl that even very dilute solutions of chlorides and silver salts give a precipitate (p. 188). In the general equation, therefore, M has to b replaced by silver and B by chlorine. If silver chlorate be prepare and be decomposed with hydrochloric acid, silver chloride and chlori acid are formed according to the equation

$$AgClO_3 + HCl = HClO_3 + AgCl,$$

in which Ag is the symbol for silver.

Silver chlorate can be obtained in the same way as sodium o potassium chlorate, by the action of chlorine on silver hydroxide.

The same principle can be carried out in various other ways, sinc every insoluble salt gives a possible combination. Indeed, for th actual preparation of chloric acid, other substances are mostly employed, especially barium chlorate and sulphuric acid. With these the same result is obtained, since barium sulphate is also a very difficultly soluble salt.

In employing this method of preparation, the amounts of the reacting substances must be determined exactly, so that neither the one nor the other shall be in excess and contaminate the chloric acid which remains behind. In the method itself, however, is contained a security against this, for the one substance must be added to the solution of the other only so long as a precipitate is formed. The clear liquid is tested with a small quantity of the first substance to see if an excess of the second has not been added, and one continues testing with the two substances alternately until a sample of the solution gives no precipitate either with the one or with the other.

* It must not be thought that in this way an "absolutely" pure solution is obtained. This would be the case only if the precipitate were absolutely insoluble, which, however, is never the case. When, however, the solubility of the precipitate is known from other measurements, the amount of impurity still present can be calculated.

The solution of chloric acid thus obtained, is a strongly acid, colourless liquid, which, although fairly stable in dilute solution, slowly decomposes into oxygen and hydrochloric acid. The latter substance acts in turn on the remaining chloric acid with formation of chlorine and water, so that oxygen and chlorine are finally obtained. Expressed in equations, we have

$$2HClO_3 = 2HCl + 3O_2$$

and

$$5HCl + HClO_3 = 3H_2O + 3Cl_2,$$

or, combined together,

$$4HClO_3 = 2H_2O + 2Cl_2 + 5O_2.$$

The decomposition takes place all the more rapidly the more concentrated the solution becomes and the higher the temperature rises. By reason of the large quantities of oxygen which are evolved in the decomposition, chloric acid is a strong oxidising agent.

Chloric acid as such finds no application, but the chlorates are largely used. Fuller information with regard to this will be given under the respective metals.

Solubility of Salts.—In order to successfully perform the above-mentioned separation of two salts by crystallisation, on the basis of difference of solubility, a knowledge of the general laws to which the solutions of solid substances are subject, is necessary. The most important of these are the following.

When a solid substance dissolves in a liquid, there is for each temperature a definite *solubility, i.e.* a definite ratio between the amounts of the dissolved substance and of the solvent. This ratio can be expressed in two ways, either by taking the total amount of the solution or only the amount of the solvent, as unit, or putting it equal to 100. The former method of calculation is the one most suitable for scientific purposes, but the latter is almost entirely used, and we shall retain it here. The *solubility* will, accordingly, be represented by the amount of solid substance which can dissolve in 100 parts of the solvent.

If less of the solid substance is brought into contact with the liquid than corresponds to the solubility, it all dissolves and the solution is called *unsaturated*, because it can still take up further quantities of the solid substance. If more of the solid substance is added, an amount dissolves corresponding to the solubility, and the excess remains undissolved. The solubility is quite independent of the amount of this excess, and the same concentration is therefore found, whether the solution is in contact with much or with little of the solid substance.

The solubility is therefore an expression of the equilibrium between the solid and the liquid portion, just as, for example, the melting point of a single substance is an expression of the equilibrium between the solid and the liquid form. In both cases, the equilibrium is independent of the relative and absolute amounts of the participating phases. This statement applies quite universally to all equilibria between different phases.

* When the solid substance is not present, one of the factors of the equilibrium is wanting, and there is no cause present to prescribe a definite concentration. From this it follows that a solution alone need not have a definite concentration. In the case of unsaturated solutions this requires no further explanation; as small quantities of the solid substance as we please can be dissolved in a given quantity of the liquid. The theorem, however, must also apply to more concentrated solutions, *i.e.* there can be solutions which contain more of the solid substance than corresponds to the condition of equilibrium in presence of the solid form.

* As a matter of fact, such solutions can be prepared in variou ways. If the solid substance is not present, they are just as stable (a least within certain limits) as the unsaturated solutions; in contac with the solid form, however, they behave in the opposite way t these. Whereas the unsaturated solutions dissolve the solid form there separates from the *supersaturated* solutions, as they are called, s much of the solid substance that the condition of saturation is agai established.

Influence of Temperature and Pressure on the Solubility —If the temperature changes, the solubility in general also changes In the case of most solid substances, the solubility increases as th temperature rises; in the case of some, however, it decreases. Th change of solubility with the temperature is usually represented by curve, the temperatures being measured towards the right, the solu bilities upwards. In Fig. 72 such curves are given for sodium chloride, potassium chloride, and potassium chlorate. The following facts can be learned from the figure.

The solubility of potassium chloride increases proportionally with the temperature, *i.e.* for equal changes of temperature, the quantity of salt contained in the saturated solution varies by equal amounts. The solubility of potassium chlorate, however, increases *more quickly* than the temperature, for, for equal differences of temperature, the changes of the solubility are all the greater the higher the temperature. The former case is represented by the straight course of the solubility curve, the latter by the bending upwards of it.

The solubility of sodium chloride is characterised by the fact that it is almost independent of the temperature, *i.e.* at different temperatures it retains almost the same value. This circumstance can be immediately recognised by the fact that the curve is almost horizontal.

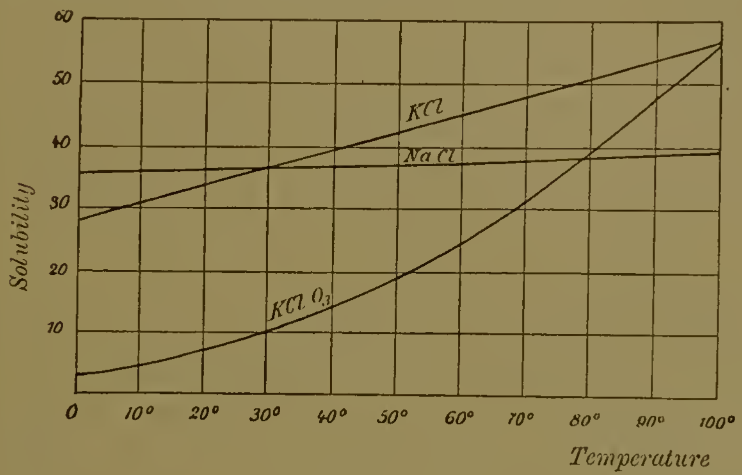


Fig. 72.

To the question as to whether the solubility could be dependent on any other circumstances besides the temperature, an answer is given by the phase law (p. 171). Since we are dealing here with two components, the solid substance and the solvent, the sum of the phases and the degrees of freedom is equal to 2 + 2 = 4. In the case of a solution in equilibrium with the solid substance, we have two phases, namely, the solution and the solid body; accordingly, there are still two degrees of freedom. One of these is disposed of by the temperature, and one still remains, and it must be possible to change the solubility by other circumstances, *e.g.* by pressure.

From experiments carried out in this connection the result has been obtained that such a variability certainly exists, but is exceedingly slight. Large pressures amounting to hundreds of atmospheres are required to bring about such a change of the solubility as can just be measured. It is admissible, therefore, for most purposes to take the possibility of this influence as little into account as in the case of the change of the melting point with the pressure.

Relation between Solubility and Heat of Solution.—The question, on what does the influence of temperature on the solubility depend, or better, is this influence related to any other property of substances, can be answered on the basis of the same principle as has already been several times applied in answer to the question as to the influences affecting equilibrium. When a system is subjected to a constraint, that process will take place which tends to counteract the constraint. If, then, the temperature of a saturated solution be raised, the equilibrium will be shifted in such a way that a reaction will take place which is accompanied by lowering of temperature. In the case, which is the most frequent, of the dissolution of the solid substance taking place with absorption of heat, and therefore with lowering of temperature, this process must result, and the solubility will increase with rise of temperature. Cases exist, however, in which heat is developed on solution, and in such cases the solubility will decrease with rise of temperature. Finally, substances which attain the condition of saturation without exhibiting heat effects, will have a solubility which is independent of the temperature.

These relations have, indeed, been demonstrated in many cases, and no contradictory case is known.

* Apparent contradictions, certainly, have made their appearance through a false application of the theory. As follows from the above exposition, it is a question of the heat which is taken up or given out when a further quantity of salt is dissolved in a solution saturated at a definite temperature. This quantity of heat must not be confused with that which accompanies the solution of a salt in the *pure* solvent, and which is usually what is measured. In the case of difficultly soluble substances, it is true, the two are not greatly different; but where the substances are soluble in large amounts, they can have not only a different value but even a different sign.

Crystallisation.—From the foregoing relations there follows the general behaviour of a solid substance and its solution. If the substance has been formed in solution it cannot separate out until its concentration has become greater than that corresponding to the point of saturation at the existing temperature. If this concentration is exceeded, the separation *can*, but does not necessarily take place, since the solution can also remain supersaturated. If, however, the separation has once started, it proceeds until there is contained in the solution only as much as corresponds to the point of saturation.

In the case more especially of substances whose solubility increases with the temperature, solutions are obtained by saturation at higher temperatures, which, on cooling, are supersaturated, and from which, therefore, the solid substance separates out. Since under these conditions the substance generally crystallises well, such a method of procedure is known as *recrystallisation*. Of the substances given in Fig. 72, potassium chlorate can be recrystallised very well from hot solutions, since the difference of solubilities at different temperatures is very great. The method is less suitable for potassium chloride, and not at all suitable for sodium chloride. For the purpose of recrystallising these substances other means must be employed by which the solid substance is caused to separate out.

* These differences of behaviour can be made clear by an experiment. If potassium chlorate be added to boiling water as long as it is dissolved, so much of the salt is deposited on cooling that the liquid forms a firm paste. From a solution of potassium chloride saturated in the heat, a much smaller amount of crystals is deposited, and from the solution of sodium chloride, practically none.

Solutions may be made to crystallise not only by change of temperature but also by diminishing the amount of solvent. In the case of volatile liquids this is best effected by evaporation. Thus, for example, by evaporating the water of the naturally occurring solutions of common salt, the salt springs, the salt contained in them is obtained in the crystalline condition. This method of *crystallisation by evaporation* is used almost more frequently than the method of crystallisation by cooling.

Behaviour of Mixed Salts.—Regularities similar to those just set forth obtain in the case where several salts, or, generally, several solid substances, are present at the same time. In this case also there corresponds to each temperature a definite condition of saturation which is independent of the relation between the amounts of the different phases. When several salts are present the solubility of each single salt, certainly, is no longer the same as when it is present alone, but they exercise a mutual influence on one another. This, however, affects only the numerical values and not the general relations.

If, now, the point of saturation of a mixed solution is exceeded, this does not, in general, occur at the same time for both salts, but the solution which is supersaturated for the one is still unsaturated with respect to the other. For this reason only the one solid substance separates out from the solution, and its separation from the other is thus effected.

For example, on evaporating a solution of any mixture of salts, only that salt will, in the first instance, separate out whose point of saturation is first reached. On withdrawing the crystals which are deposited from the solution, the substance is obtained in the pure state. Only when the point of saturation of the other substances is reached do these separate out along with the first, and mixtures are obtained.

In such cases the separation can generally be carried further by making use of the different variation of the solubilities with the temperature. For example, if a solution of potassium chloride and potassium chlorate, from which pure chlorate first separated, has reached the point at which both salts would be deposited together on further evaporation, it is only necessary to concentrate the solution at a higher temperature. The chlorate is then relatively the more soluble and the liquid deposits chloride; if, then, saturation with respect to chlorate is again almost reached, a mixture will be obtained on cooling which contains much chlorate and little chloride, and by redissolving and crystallising, these can be for the greater part separated. By repeating the separations the task can finally be so far accomplished that the residue of unseparated salts can be neglected.

The method of separation to be pursued in individual cases depends accordingly on a knowledge of the various solubilities. The general relations we have explained allow in each case of the most appropriate method being ascertained.

Perchloric Acid.—A further step between chlorate and oxygen is met with on carefully heating potassium chlorate or another chlorate. A portion of the salt, the amount of which depends on external circumstances, and especially on the nature of the vessel and the presence of solid impurities in the salt, decomposes into oxygen and potassium chloride; another portion, however, passes into a compound richer in oxygen.

If potassium chlorate is kept heated to a temperature somewhat above its melting point, the evolution of oxygen, which is at first considerable, becomes slower and ceases long before the oxygen present has been expelled. At the same time solid crusts begin to separate from the fused salt; and when the evolution of gas ceases, the salt has also again become solid, although the temperature is not lower.

The salt mixture produced can be readily separated by crystallisation into potassium chloride, which is readily soluble, and a new salt whose solubility in water is very small. It is obtained almost pure by extracting the finely powdered mixture with cold water, whereby most of the potassium chloride is removed, and dissolving the residue in hot water. On cooling, the new salt crystallises out.

Analysis shows it to be composed of potassium, chlorine, and oxygen according to the formula $KClO_4$, and it is, therefore, the potassium salt of a new acid, called *perchloric acid*. The salts of this acid are the *perchlorates*.

Just as the potassium salt is obtained from the chlorate, the free acid is similarly formed from chloric acid when this is evaporated by heating. By this treatment, a portion of the acid decomposes into water, chlorine, and oxygen (p. 213); another portion, however, takes up oxygen from the decomposed portion and passes into perchloric acid.

The process in the case of the potassium salt is represented by the following equation:—

$$4KClO_3 = 3KClO_4 + KCl.$$

In the case of the acid the equation is the same except that K is replaced by H.

Although the transformation is accompanied by evolution of oxygen, this does not seem to be essential, for, by careful heating, it can be brought about without the escape of oxygen.

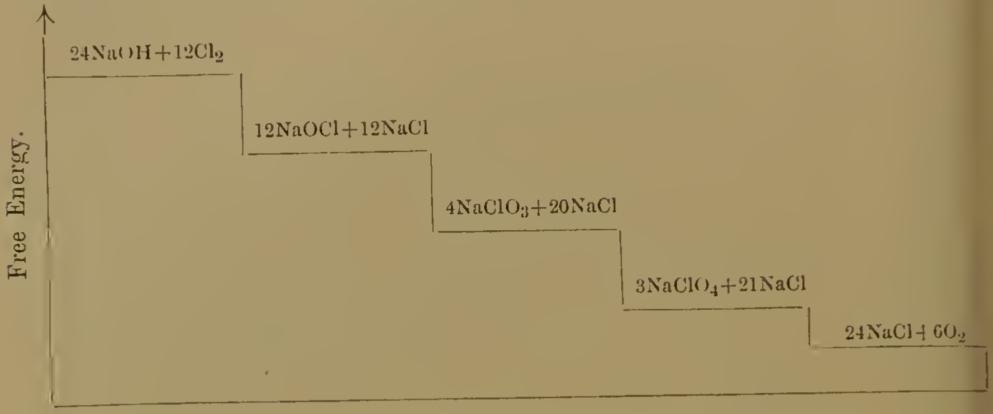
Properties of Perchloric Acid.—Perchloric acid is much more stable than the other oxy-acids of chlorine. Whereas the hypochlorites, when treated with hydrochloric acid, are converted instantaneously, and the chlorates pass readily into water and chlorine, this decomposition does not take place in the case of the perchlorates; potassium perchlorate can be evaporated with hydrochloric acid without decomposition and evolution of chlorine taking place. For this reason it is possible to distil perchloric acid and to obtain perchloric acid by the distillation of perchlorates with acids, although the boiling point of the acid is fairly high.

The properties of perchloric acid differ markedly according as the acid is completely anhydrous or contains a little water. Prepared from potassium perchlorate by distillation with sulphuric acid, it is obtained as an oily liquid, boiling at over 200°, which is exceedingly stable and exhibits no oxidising properties. It contains 70 per cent pure acid and 30 per cent water. If this liquid is mixed with double its volume of sulphuric acid and again distilled, the water is retained by the sulphuric acid and the pure acid, $HClO_4$, passes over as a strongly fuming liquid. If the distillation is continued, an aqueous acid distils over and combines in the receiver with the anhydrous acid, forming a crystalline hydrate of the composition $HClO_4 + H_2O$. From this, the pure acid can be again obtained by careful distillation. The pure acid is colourless, very volatile, has the density 1·78, and decomposes with extreme readiness, so that on being brought in contact with oxidisable substances it generally explodes with violence. When placed in water it dissolves with a hissing sound and great evolution of heat, forming a very stable solution which, on evaporation, again yields the oily, stable, 70 per cent acid.

The cause of this great divergence of properties lies in the fact that the aqueous acid contains ions, whereas the anhydrous acid does not (p. 179). The ions are much more stable than the free acid, and for this reason, also, the salts of perchloric acid do not show any of the readiness to decompose which is manifested by the free acid.

In perchloric acid we have another example of solutions whose boiling point changes with the composition in such a way that it has a maximum value at a definite concentration. The relations discussed in detail in the case of hydrochloric acid (p. 182) are again met with here; the fact, also, that the concentrated acid fumes in moist air, is further evidence of the similarity.

The succession of the products of interaction of chlorine and caustic soda, which was indicated on p. 209, must, in accordance with what has been said, be completed as follows :—



For the sake of shortness, the $12H_2O$, produced in the passage to the second stage, have been omitted, since they take no further part in the transformations.

Other Oxygen Compounds of Chlorine.—The substances hitherto described do not exhaust the possible number of compounds of chlorine with hydrogen and oxygen, although the substances still to be treated are of inferior importance to those already mentioned.

If a chlorate is decomposed with a strong acid, *e.g.* sulphuric acid, chloric acid is first formed, in accordance with the general scheme. This substance is, however, not stable in the anhydrous condition, and immediately undergoes decomposition, in accordance with the equation

$$4HClO_3 = 2H_2O + 4ClO_2 + O_2.$$

In other words, water is formed from the components of the acid, this being necessary for the production of the more stable ions of the remaining chloric acid.

The compound ClO_2, formed at the same time, bears the name of chlorine dioxide or chlorine peroxide, and appears as a yellow-brown gas which can be condensed to a similarly coloured liquid at a temperature under 10°. Both gas and liquid are extremely explosive. This can be shown by placing on the bottom of a wide-mouthed bottle of 2 to 3 litres capacity, a small dish containing some potassium chlorate and allowing a few drops of concentrated sulphuric acid to fall on this. The yellow gas is evolved with a peculiar crackling sound due to small explosions. If a warm metal rod, the temperature of which can be much below that of the visible red-heat, be introduced some moments later into the gas, this decomposes with loud detonation into chlorine and oxygen.

Chlorine peroxide is not the anhydride of any definite acid, but, when brought in contact with caustic soda, yields sodium chlorate and the salt of a new acid. The process takes place in accordance with the equation

$$2ClO_2 + 2NaOH = NaClO_3 + NaClO_2 + H_2O.$$

The salt $NaClO_2$ is called *sodium chlorite*, and the acid *chlorous acid*. It is little known, and its salts, which are mostly very unstable, have as yet found no application.

What position the chlorites occupy in the transformation series and order of stability of the oxygen compounds of chlorine, is not yet known; to all appearance it is a fairly high one.

* **Thermochemical Relations of the Oxygen Compounds of Chlorine.**—As can be conjectured from the explosive properties of most of the substances of this group, the compounds contain, in general, considerably more energy than the elements, and therefore decompose into these with evolution of heat. Even if the differences of the *total energy* found here do not coincide with those of the *free energy* (p. 208), still the two agree with one another so far, both with regard to sign and order of magnitude, that in absence of a more exact knowledge of the latter, the former may be taken as the basis of our considerations.

Chlorine monoxide decomposes with evolution of heat into its elements, and must therefore absorb heat if formed from them. The equation is:—

$$2Cl_2 + O_2 = 2Cl_2O - 2 \times 74\ kj.$$

The gas dissolves in water with an evolution of 39 *kj*; the formation of a solution of hypochlorous acid from water, chlorine, and oxygen would therefore absorb 35 *kj*. Since from Cl_2O, 2HOCl are formed, there are – 17·5 *kj* for each molecule, and we have the equation

$$2Cl_2 + O_2 + aq. = 4HOCl\ aq. + 4 \times -17{\cdot}5\ kj.$$

If, however, we consider the formation of hypochlorous acid from chlorine, oxygen, and *hydrogen*, we must add to the above the heat of formation of water. Adding to the last equation

$$2H_2 + O_2 = 2H_2O + 2 \times 286\ kj$$

and dividing by 2, we obtain

$$Cl_2 + O_2 + H_2 + aq. = 2HOCl\ aq. + 2 \times 125\ kj.$$

In this case, therefore, there is a considerable development of heat. For this reason hypochlorous acid never decomposes into chlorine, oxygen, and hydrogen, but only into chlorine, oxygen, and water.

If, from the equation for the heat of formation of hydrochloric acid,

$$Cl_2 + H_2 + aq. = 2HCl\ aq. + 2 \times 164\ kj,$$

that for hypochlorous acid be subtracted, there follows

$$HOCl\ aq. = HCl\ aq. + O + 39\ kj,$$

that is to say, when hypochlorous acid decomposes into hydrochloric acid and oxygen, 39 *kj* are developed. When, therefore, hypochlorous acid acts as an oxidising agent, the heat which is thereby developed is, for each combining weight of oxygen, greater by 39 *kj* than if the oxidation took place with free oxygen. This would suggest that hypochlorous acid, quite apart from its greater velocity of reaction, would be a stronger oxidising agent than free oxygen, and that it would be capable of oxidising substances not oxidised by this.

This makes us return to the point mentioned on p. 207. Since the decomposition of hypochlorous acid into oxygen and hydrochloric acid takes place with considerable diminution of the free energy, it can be used for the purpose of preparing oxides which could be formed from oxygen only with increase of the free energy, and which, therefore, are not directly formed from it. Since the taking up of oxygen from the hypochlorous acid by the substances in question necessarily takes place simultaneously with the decomposition of the acid, we have here the "coupling" which has been characterised as a presupposed condition in using the free energy of one process to render another process possible (p. 203). Thus, for example, dilute hydrochloric acid can be easily oxidised to chlorine and water by means of hypochlorous acid (p. 206), a process which is not possible with free oxygen, because the reverse formation of free oxygen from chlorine and water takes place (p. 169).

The heat of formation of *chloric acid* is given by the following equations:—

$$H_2 + Cl_2 + 3O_2 + aq. = 2HClO_3\,aq. + 2 \times 100\ kj,$$
$$2Cl_2 + 5O_2 + aq. = 4HClO_3\,aq. - 4 \times 43\ kj.$$

From this we obtain the heat evolved in oxidation by means of chloric acid:—

$$HClO_3\,aq. = HCl\,aq. + 3O + 64\ kj.$$

There is a heat evolution, therefore, of 21 *kj* for each combining weight of oxygen. This number is considerably smaller than in the case of hypochlorous acid, which is in agreement with the smaller oxidising power of chloric acid.

For *perchloric acid*, the corresponding equations are:—

$$H_2 + Cl_2 + 4O_2 + aq. = 2HClO_4\,aq. + 2 \times 161\ kj$$
$$2Cl_2 + 7O_2 + aq. = 4HClO_4\,aq. + 4 \times 18\ kj$$
$$HClO_4\,aq. = HCl\,aq. + 4O - 3\ kj.$$

In all three equations the greater stability and feebler oxidising action of perchloric acid finds expression.

* **The Combining Weight of Chlorine.**—For the purpose of determining the combining weight of chlorine with sufficient exactness, a somewhat indirect method has been found necessary. First,

potassium chlorate was converted, by heating, into potassium chloride and oxygen. Calculating, in accordance with the equation

$$KClO_3 = KCl + 3O,$$

how much potassium chloride is combined with $3 \times 16 = 48$ parts by weight of oxygen, the number obtained represents the combining weight of potassium chloride referred to oxygen equal to 16. Since, now, every gram of potassium chlorate on ignition leaves a residue of 0·6085 gm., losing, therefore, 0·3915 gm. oxygen, we have the proportion

$$KCl : 48 = 0·6085 : 0·3915,$$

which gives for the combining weight of potassium chloride, $KCl = 74·59$.

Next, it was determined how much silver chloride could be obtained from a given amount of potassium chloride. Since one combining weight of chlorine is contained in each salt, the ratio of the weights in which the one is formed from the other is also equal to the ratio of their combining weights. It was found that from each gram of potassium chloride, 1·9224 gm. silver chloride was obtained. Hence,

$$AgCl : 74·59 = 1·9224 : 1,$$

from which we find, $AgCl = 143·39$.

Lastly, a weighed quantity of silver was converted into silver chloride. Each gram of silver yielded thereby 1·3284 gm. silver chloride, taking up, therefore, 0·3284 gm. chlorine. Calculating with the aid of this relation how much chlorine is contained in one combining weight of silver chloride, the combining weight of chlorine is found from the proportion

$$Cl : 143·39 = 0·3284 : 1·3284$$

to be, $Cl = 35·45$.

From these determinations, we can further obtain the combining weights of silver and potassium. Subtracting the combining weight of chlorine from the combining weight of silver chloride which was found equal to 143·39, there follows, $Ag = 107·94$. A similar calculation in the case of potassium chloride yields $K = KCl - Cl = 74·59 - 35·45 = 39·14$.

The reason that such an indirect method has been employed, is due to the fact that the simple oxygen compounds of chlorine cannot, on account of their unstable nature, be prepared sufficiently pure nor analysed with sufficient exactness. The transformations above described, however, can be performed with very great exactness, and this is the determining reason for preferring the indirect to the direct method.

CHAPTER XI

BROMINE, IODINE, FLUORINE

A. *Bromine*

General.—Bromine is an element which closely resembles chlorine in all its relations. Discovered by Balard in 1826, it has since then been found to be, indeed, very widely distributed, but it is met with in much smaller amount than chlorine. Its compounds occur in small quantities in sea-water, and are contained, therefore, in the residues left on the artificial or natural evaporation of this. From the residues which are obtained by the latter process, and which, in Germany, chiefly occur near Stassfurt, bromine is obtained and sent into the market.

Bromine is a dark, brown-red liquid, transparent only in thin layers and having a density 3·1. It boils at 60°, and even at room temperature possesses a considerable vapour pressure. Bromine, therefore, evaporates very quickly even under ordinary conditions; and as its vapour has a very unpleasant smell and a strong corrosive action on the mucous membrane, care must be observed in working with it. Bromine solidifies at – 7° to – 8° to a dark-coloured, crystalline mass.

The vapour of bromine is very heavy. If a small bulb filled with bromine be broken, or if, by means of a pipette, a drop of bromine be placed at the bottom of a large, empty bottle, it is seen that the brown-yellow vapour produced remains at the bottom and sways heavily when the bottle is moved. Only after standing undisturbed for a considerable time does the bromine vapour slowly ascend into the upper parts of the bottle, in accordance with the general law of the diffusion of gases, which states that equilibrium occurs only when the partial pressure of each gas or vapour present has become equal throughout the whole space (p. 93).

* If the same experiment be repeated in a bottle filled with hydrogen, diffusion takes place much more rapidly; and by performing two parallel experiments with air and with hydrogen side by side, the great difference in the height of the bromine will be perceived ever

after 5 to 10 minutes. This appears remarkable, since the difference of density as compared with hydrogen is much greater than that compared with air, and, therefore, the work to be performed against gravity is also greater. That, nevertheless, bromine vapour and hydrogen mix more quickly is due to the fact that diffusion proceeds more rapidly in hydrogen because, in this case, the mutual friction of the gases is less. The velocity of diffusion obeys, to some extent, though by no means exactly, the same law as the velocity of effusion (p. 95), and is, in the case of hydrogen, about four times as great as in air.

From determinations of the density of bromine vapour, its molar weight has been found to be 160, or five times as great as that of oxygen. Bromine vapour is, therefore, 5·5 times as heavy as air. Since the combining weight has been found to be half as great (the exact figure being 79·96), the composition of bromine vapour is represented by the formula Br_2. At very high temperatures, the molar weight becomes somewhat less. Since similar relations are found and have been more fully investigated in the case of iodine, we shall discuss this phenomenon at that point.

Bromine dissolves in water, forming a yellow to brown coloured liquid, which possesses the smell of bromine and can be used in place of pure bromine when only a small quantity of the substance is required. The solution, saturated at room temperature, contains about 3 per cent of bromine. If the water contains saline compounds of bromine in solution, more bromine is dissolved, readily decomposable compounds of bromine being formed which, in most of their relations, behave like free bromine. These relations, also, will be discussed more fully under iodine.

From the aqueous solution of bromine (bromine water) there separates out, on cooling, a solid hydrate which behaves quite similarly to chlorine hydrate (p. 170).

Hydrogen Bromide.—With hydrogen, bromine forms a compound, HBr, which is very similar to hydrogen chloride. The reaction between the elements, however, is not nearly so vigorous as in the case of chlorine. If bromine vapour be mixed with hydrogen, no sudden reaction takes place either on passing an electric spark or on exposing the mixture to sun-light; only a partial combination of the gases occurs. The reaction can be accelerated by employing catalytic agents, and for this purpose, platinum and the metals like it have been found to be specially active. If a suitable mixture of hydrogen and bromine vapour be passed through a gently heated tube filled with finely divided platinum, the issuing gases contain large quantities of hydrogen bromide, and, by suitable arrangement, the reaction is practically complete.

Hydrogen bromide is obtained more easily, and in a manner more suited for experimental purposes, by the simultaneous action of bromine and phosphorus on water. The chemical reaction which here takes place cannot be completely explained till we come to phosphorus; suffice it to indicate that a partition of the elements of water results. The oxygen combines with the phosphorus and the hydrogen with the bromine. Bromine alone is not able to decompose water, as this would be associated with an increase of the free energy (p. 208). If this reaction, however, be joined with another in which a considerable diminution of the free energy occurs, so that over the whole process there is a diminution of the free energy, the reaction becomes possible. The auxiliary process in this case is the combination of oxygen with phosphorus which, as we know (p. 63), is accompanied by the liberation of large quantities of energy.

The experiment is carried out as follows. Red phosphorus along with some water is placed in a small flask through the cork of which pass a dropping-funnel containing bromine, and a delivery tube (Fig. 73). To this is connected a U-tube filled with moistened red phosphorus spread out on pieces of glass. The purpose of this is to convert any bromine vapour which may escape from the flask also into hydrogen bromide. On allowing the bromine to drop slowly into the flask, a violent reaction, accompanied by flashes of light, takes place, and from the end of the U-tube a colourless gas escapes which forms dense fumes in the air and is absorbed with extreme readiness by water. It thus behaves very similarly to hydrogen chloride.

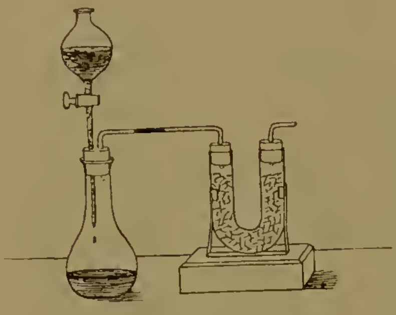


FIG. 73.

The gas cannot be collected satisfactorily over mercury, since it is decomposed by this metal, mercury bromide and hydrogen being formed; still the reaction does not proceed rapidly. On account of its great density it can be collected, like chlorine, by displacement of the air. In this case the appearance of a thick mist at the mouth is the sign that the vessel is full.

The molar weight of hydrogen bromide is 81, corresponding to the formula HBr. The gas shows noticeable deviations from the simple laws.

By pressure and cold, hydrogen bromide can be converted into a liquid which boils at − 73° and, like liquid hydrogen chloride, has only a comparatively slight reactivity.

The Solution of Hydrogen Bromide.—An aqueous solution of hydrogen bromide can be obtained by connecting to the generating apparatus (Fig. 73) the arrangement described on p. 180 for the absorption of a gas. The solution, saturated at 0°, contains 80 per cent of hydrogen bromide; it is very strongly acid, fumes in the air, and has a density of 1·5. More dilute solutions do not fume so much, and the 48 per cent solution is in the same condition as the 20 per cent solution of hydrogen chloride; it distils over with unchanged composition. The relations described in the case of hydrogen chloride (p. 182) are repeated quite similarly in the case of hydrogen bromide, so that they need not be again described.

The characteristic reactions of acids are displayed in the same way by hydrogen bromide as by hydrogen chloride, so that equivalent solutions of the two acids behave almost identically, not only qualitatively but also quantitatively. Hydrobromic acid, therefore, belongs to the strongest acids, and even in moderately dilute solutions is largely dissociated into its ions.

Hydrobromic acid acts on the metals in the same way as hydrochloric acid: hydrogen is evolved and the bromides of the metals are formed. These are identical with the compounds which are obtained by the action of the hydroxides of the same metals on hydrobromic acid, water being simultaneously formed, and with those obtained by the direct action of bromine on the respective metals.

In the latter case the action is, in general, not so energetic as in the case of chlorine, but the difference is not very great. An idea of this is obtained by introducing a piece of thin rolled metallic tin (tinfoil), such as is used for wrapping up chocolate and such things, into liquid bromine contained in a test-tube. The two elements immediately combine with the production of a dark red flame and the evolution of thick vapours. On account of the poisonous properties of these, the experiment must be carried out in a fume chamber with good draught.

The aqueous solutions of hydrobromic acid and of most of the metallic bromides contain bromine in the ionic condition. In this form it exhibits the general properties of ions of electrolytic conductivity, and the numerical values of this generally agree very closely with those of the equivalent chlorides. A reaction with silver solutions is also given, and the precipitate of silver bromide which is produced by silver salts in all solutions containing bromidion is very similar to silver chloride in appearance, but is of a yellowish colour and is much less soluble than silver chloride. The reactions by means of which the two substances can be distinguished from one another will be given under silver.

When chlorine is passed into solutions containing bromidion, an exchange of conditions takes place: the chlorine passes into chloridion and bromidion into bromine. For this reason, all such solutions on addition of chlorine water become yellow in colour, and since this coloration is quite visible even with a very small concentration of bromine, it serves as a means of identification or reagent for bromidion. Since chloridion cannot, of course, react with chlorine, this reagent can also be used to distinguish between bromidion and chloridion, and for the identification of the former in presence of the latter.

Employing a dash to indicate the ions, as mentioned on p. 199, the reaction in question would be written,

$$2Br' + Cl_2 = 2Cl' + Br_2.$$

No bromidion, of course, can be present in solution unless an equivalent amount of some cation be also present; the latter, however, plays no part in the process, which takes place in the same way whatever the cation may be.

This reaction is used for the preparation of bromine from the liquids in which bromine compounds occur naturally, more especially from the mother liquors obtained in the working up of the potassium salts at Stassfurt (p. 52). All these salt solutions contain the bromine in the ionic form, and on passing in chlorine and distilling the liquid, the readily volatile bromine passes over with the steam. The chlorine required for this purpose can also be prepared in the liquid itself by adding a hypochlorite (*e.g.* bleaching-powder), for example, and then hydrochloric acid. By means of a preliminary determination of the amount of bromine in the liquors, however, care must be taken rather to add too little than too much chlorine, in order that the bromine produced be not contaminated with chlorine.

Oxy-acids of Bromine.—Bromine is readily dissolved by a solution of caustic soda, the liquid remaining bright yellow in colour. Besides sodium bromide, the liquid then contains *sodium hypobromite*. The reaction agrees entirely with the corresponding one in the case of chlorine, for it takes place according to the equation

$$2NaOH + Br_2 = NaBr + NaOBr + H_2O.$$

The solution produced is used in the laboratory. By reason of the oxygen of the hypobromite, it has as powerful an oxidising action as hypochlorite solution.

The corresponding acid, hypobromous acid, HOBr, can also be prepared in dilute aqueous solution. It is very similar to hypochlorous acid.

On standing some time, especially when an excess of bromine is present, the solution passes into one containing *sodium bromate* along with bromide. In this case also, it is better to use a solution of potassium hydroxide. On adding bromine to such a solution without cooling, until its colour is permanent, the potassium bromate separates out at once in the form of a crystalline precipitate. Neglecting the intermediate, hypobromite stage, the reaction is

$$6KOH + 3Br_2 = 5KBr + KBrO_3 + 3H_2O.$$

From this salt bromic acid, $HBrO_3$, can be obtained in aqueous solution in the same way as chloric acid was obtained from chlorate.

It is very similar to chloric acid, only still more easily decomposed. It is not known in the anhydrous condition.

A perbromic acid has not yet been prepared, and no oxygen compound of bromine is known corresponding to chlorine monoxide and chlorine dioxide. In general, the compounds of bromine containing oxygen decompose more easily than the corresponding chlorine compounds.

The *combining weight of bromine* has been determined in a manner similar to that used for chlorine. It amounts to 79·96, or almost exactly 80. The deviation from the round number, however, is not due to experimental error, but has been proved beyond doubt.

B. *Iodine*

General.—Iodine is allied to chlorine and bromine, and forms a third similar element. Of the three, it has the highest combining weight, amounting to 126·86, and its properties show deviations from those of bromine chiefly in the same direction as those of bromine deviate from chlorine.

At ordinary temperatures, iodine is a solid, crystalline substance of a purple-black colour with an indication of metallic lustre. Its density is 5. At 114° it melts to a deep brown liquid. Even at ordinary temperatures it emits some vapour, which can easily be recognised by its reddish-purple colour when a little iodine is contained in a fairly large vessel. Iodine, however, does not boil till 184°.

Iodine vapour is of a fine violet colour. For the purpose of observing this colour and at the same time also the great density of iodine vapour, a large, round-bottomed flask is strongly heated in a large flame, being kept diligently turned the while, and a few crystals of iodine are then thrown into the hot flask. The iodine is at once converted into a vapour of a dark violet colour, which remains at the bottom and which, when the vessel is moved, shows itself in a high degree subject to the force of gravity.

The density of iodine vapour is very considerable, being about nine times as great as that of air. The molar weight is 254 and the vapour has, therefore, the formula I_2. An account of its behaviour at higher temperatures will be given presently.

In water, iodine is only sparingly soluble, but still sufficiently for the brown colour with which it passes into solution to be detected in fairly thick layers. If a salt-like iodide is present in the water, much larger quantities are dissolved with a brown colour. This is due to the formation of an ion I_3', as will be immediately discussed.

In other liquids, iodine is generally more soluble. In spirit of wine it dissolves with a brown colour similar to that of the aqueous iodide solutions. This solution is used in medicine, and is called tincture of iodine. Other solvents, such as carbon disulphide and chloroform, dissolve it with a fine violet colour similar to that of the vapour. On what these differences of colour depend is as yet unknown, but it appears that in the brown solutions easily decomposable compounds are formed between iodine and the solvent.

If an aqueous solution of iodine is shaken with carbon disulphide,[1] the colour of the iodine disappears from the aqueous solution, and the carbon disulphide is coloured purple. The iodine, therefore, leaves the water in order to dissolve in the carbon disulphide. This is an example of a general phenomenon which is subject to definite laws.

The Law of Distribution.—If to two liquids A and B, which are not (or rather, are only slightly) miscible with one another, a substance be added which is soluble in both, this substance will, in general, dissolve in both liquids and a state of equilibrium will be established. This state is determined by the law that *the substance is distributed between the two solvents in such a way that the ratio of its concentration in each is constant.*

This ratio is independent of the amounts of the two solvents, and of the absolute concentration, at least within definite limits, and depends only on the nature of the three substances and on temperature.

For example, iodine is distributed between water and carbon disulphide in the ratio 1 : 600. If, then, any quantities whatever of water, iodine, and carbon disulphide are shaken together and the two solutions then investigated, there will be found in each cubic centimetre of the carbon disulphide solution, 600 times as much iodine as in 1 cc. of the aqueous solution.

As is evident from these numbers, the concentration in carbon disulphide is very much greater than in water; for this reason, also, the greater part of the iodine passes, as the experiment shows, into the former, when an aqueous solution of iodine is shaken with carbon disulphide.

This law holds only for the iodine present in the elementary state, and not for any compounds of iodine that may be present. If carbon disulphide be rendered of a deep violet colour with iodine and the solution then shaken with a solution of caustic soda, the violet colour disappears and the iodine passes into the aqueous solution. Here, however, it no longer exists as iodine, but has formed salts with the caustic soda.[2] If hydrochloric acid be added to the solution, by which means free iodine is again formed, and the mixture be shaken, the carbon disulphide again becomes violet in colour.

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[1] Carbon disulphide is a compound of sulphur and carbon, and forms a heavy, colourless liquid which does not mix with water.

[2] The reactions which take place here agree entirely with those given by chlorine or bromine with caustic soda, and the reader is, therefore, referred to the explanation of them given previously (p. 204).

Iodine Vapour.—It has already been mentioned that the vapour of iodine has the molar weight 254. This value holds for temperatures above the boiling point up to about 500°. If the temperature be raised still higher, the iodine vapour expands more than a normal gas, and its molar weight, therefore, becomes smaller. The deviation becomes all the greater the higher the temperature is allowed to rise. At 1500°, finally, the half value is reached, and a further elevation of the temperature has no longer any effect.

This statement is true only when the pressure is equal to one atmosphere. If it is less, too small densities are found even at lower temperatures, and the half value is sooner reached. At temperatures above this, however, the molar weight again remains constant. These relations are made clear in Fig. 74. The molar weights are measured downwards, and the temperatures to the right. The numbers placed beside the curves give the pressures.

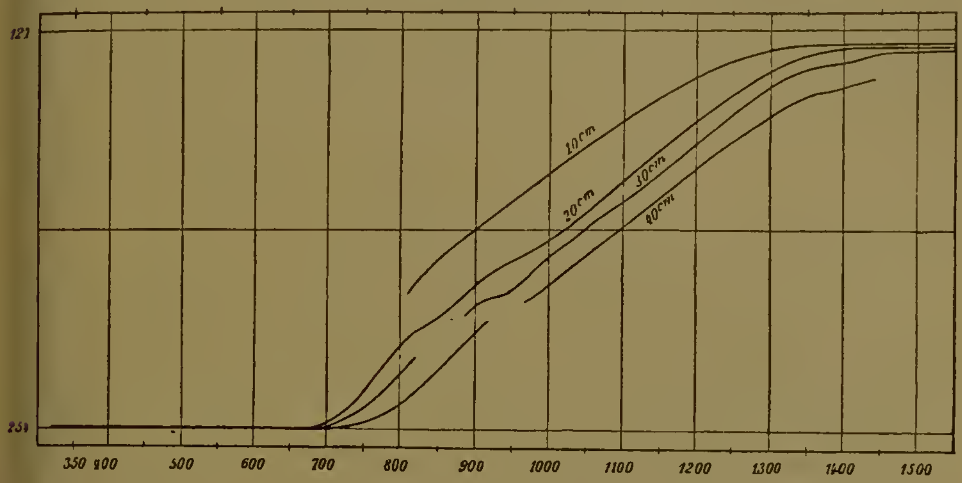

FIG. 74.

The above facts show that when iodine vapour is heated, a transformation of the vapour I_2 into I takes place, according to the equation $I_2 = 2I$. Such a decomposition of one substance into simpler substances is called *dissociation*. From the fact that the decomposition increases with rise of temperature, it is to be concluded that heat is absorbed in the process, in accordance with the repeatedly expressed general principle of resistance to change. Since the second form would, under the same pressure, occupy double the volume of the first, and, therefore, if the volume is the same, would exert twice the pressure, the transformation of I_2 into 2I would, at constant volume, cause an increase of the pressure. From this fact it can be concluded, on the ground of the same general principle, that the decomposition will be promoted by diminution of pressure, since the decomposition opposes the latter. This conclusion is borne out by the experiments represented in Fig. 74.

Compared with I_2, the substance I must be regarded as a new substance with different properties. Owing to the difficulty of investigation at such high temperatures, it has hitherto been impossible to determine these differences quantitatively. It has, however, been stated that a change in the colour of the vapour has been observed.

Starch Iodide.—Elementary iodine in the pure state, whether as vapour or in solution, is, even of itself, distinguished by its strong colour. Still smaller quantities than can be detected by the colour of the free iodine can be detected by the colour of a remarkable compound which iodine forms with *starch.*

Starch is an organic substance (that is, a substance containing carbon) composed of carbon, hydrogen, and oxygen, which occurs very widely distributed in plants, collected chiefly in the seeds or the equivalent portions of the vegetable organism. It is prepared mostly from potatoes and from wheat, and is obtained in the form of a white powder which is insoluble in cold water, but in hot water swells up to a gelatinous mass. If much water be taken, say, a hundred times as much as the weight of the starch, a liquid is obtained which can be filtered hot from the undissolved cell-walls, and which then appears clear and remains liquid.

This solution of starch, now, has the property of yielding a fine blue colour with free iodine. This coloration is exceedingly strong. The very feebly brownish coloured solution obtained by shaking iodine with water, becomes of a dark blue colour with starch solution, and liquids somewhat richer in iodine are rendered opaque. The compound which is here formed contains the iodine only very feebly united; it reacts in almost every respect like free iodine, and it is therefore employed in many chemical reactions in which iodine is produced or used up, as an indicator for the first or for the last traces of iodine.

If a solution of starch iodide, as the blue substance is called, is warmed, it becomes colourless at a temperature a little below the boiling point, exhibiting only the feebly brownish colour of iodine. On cooling, the blue colour again appears, showing that the compound is again formed from its components.

* This experiment can be rendered very clear if only the lower portion of the colourless solution, obtained by heating in a test-tube, be cooled by partially immersing the tube in cold water. Only this portion will then become blue, and as the cooled liquid is the specifically heavier, it will remain undisturbed at the bottom and the transition is fairly abrupt. In proportion as the solution cools, the blue colour gradually moves upwards.

This colour phenomenon serves for the detection both of iodine and of starch, and has, for both purposes, a great value.

Hydrogen Iodide.—Iodine and hydrogen unite to form hydriodic acid, which has the formula HI in accordance with the density 128.

Like the other halogen hydracids, it is, at ordinary temperatures, a colourless gas. Its liquefaction, however, under atmospheric pressure, takes place even at − 34°.

The union of the two elements is still less stable than in the case of hydrogen bromide. If a mixture of hydrogen and iodine vapour in equal volumes be heated, only a portion of the mixture combines to form hydrogen iodide, the other portion remaining uncombined. This proportion, also, is not altered by adding platinum sponge; the final, invariable state will only be very much more quickly reached. This point varies somewhat with the temperature; at 520°, 76 per cent of the mixture combines.

Conversely, already formed hydrogen iodide, when heated, partially decomposes into iodine and hydrogen, the mixture finally having, indeed, exactly the same composition as before. In this case the presence of platinum sponge accelerates the decomposition just as in the former case it accelerated the combination, in conformity with the general law of catalytic acceleration.

In accordance with the formula

$$H_2 + I_2 = 2HI,$$

two volumes of the compound are produced from two volumes of the mixed gases; the reaction, therefore, takes place without change of volume. Now, we have just seen (p. 231) that a diminution of the pressure promotes that reaction which, at constant volume, would be accompanied by increase of pressure. On attempting to apply this rule here, the difficulty arises that neither of the two possible reactions—neither the formation nor the decomposition of hydrogen iodide—would cause an increase of pressure. The conclusion to be drawn from this is that in this case change of pressure has *no* influence on the chemical equilibrium. This conclusion has been confirmed by experiment.

This case can be generalised, and we can enunciate the rule: *If definite states are not altered by given processes, a change in these states has, conversely, no influence on the processes.* With the help of this rule, conclusions can sometimes be drawn which are as surprising as the rule is simple.

Hydrogen iodide can be prepared, similarly to hydrogen bromide, by means of phosphorus and water, as well as by heating iodine and hydrogen in the presence of platinum. The reaction is in this case much less violent. Red phosphorus, water, and iodine can be mixed n the order given, in the proportions 1 : 4 : 15, without any considerble reaction taking place; on heating, hydrogen iodide is then evolved, nd can be collected without difficulty by displacement, as it is four imes heavier than air.

On account of the readiness with which it decomposes, almost all ubstances which combine with hydrogen act on hydrogen iodide. If he heavy gas be poured into a cylinder containing chlorine, a flame appears and the cylinder is filled with the violet vapour of iodine, hydrogen chloride being formed at the same time. Mixed with oxygen or air and ignited, hydrogen iodide burns, iodine separating out and water being formed. Hydrogen iodide acts similarly on numerous other substances, so that it can be employed in many cases for the introduction of hydrogen into other substances. It may also be successfully used for the removal of oxygen from compounds, the oxygen combining with the hydrogen of the hydrogen iodide to form water. In this case the addition of phosphorus is useful in order to regenerate hydriodic acid from the iodine and water formed.

Hydrogen Iodide and Water.—From the mere fact tha hydrogen iodide fumes strongly in air, it can be concluded tha it will behave towards water in exactly the same way as the othe halogen hydracids. As a matter of fact, it dissolves very abundantly in water. The solution saturated at 0° has a density of nearly 2, an contains about 90 per cent of hydrogen iodide. The "constant solution contains 57 per cent of hydrogen iodide and boils at 126°.

The aqueous solution of hydrogen iodide shows the genera properties of acids in exactly the same degree as the two othe halogen hydracids; it is dissociated to the same extent into ions and its action as an acid is, in consequence, not more feeble tha that of the other acids. The strength of the acid, *i.e.* its aci character, is by no means dependent on the stability of the compoun itself, but only on the degree of ion formation. On account of th lower volatility of aqueous hydriodic acid as compared with the tw other acids, hydriodic acid can even decompose the salts of these when sodium chloride is evaporated with hydriodic acid, sodium iodid is left behind, in accordance with the equation $NaCl + HI = NaI + HC$ The reaction has to be explained in the manner set forth on p. 20 according to which the most volatile of the possible compounds, i this case hydrochloric acid, escapes and makes it possible for th reaction to proceed.

On allowing an aqueous solution of hydrogen iodide to stand i the air, it speedily turns brown, and in course of time the hydroge iodide disappears and solid iodine separates out in fine crystal This change takes place in accordance with the equation $4HI + O_2 = 2H_2O + 2I_2$, *i.e.* the hydrogen iodide is oxidised by the oxygen of th air and passes into water and iodine. The liberated iodine at fir remains dissolved in the liquid, but in proportion as the hydrog iodide disappears, the solvent power also diminishes and the iodi separates out in the solid state.

The question must arise why the iodine is soluble in dilu hydriodic acid while it is almost insoluble in pure water. Oth acids, such as dilute hydrochloric acid, do not dissolve it to a great extent than water.

The answer to this question is that the iodine can combine wi

he iodidion of the hydriodic acid to form the ion I_3', which is coloured
rown. The combination does not take place completely, about half
f the iodidion remaining uncombined. Hence, about as much free
dine dissolves in the solution of dilute hydriodic acid as there is
dine already present in the form of iodidion. In more concen-
ated solutions, however, the solubility of the iodine is considerably
reater.

From what has been said, it follows that iodine must dissolve
the same extent in the solutions of all metallic iodides capable
f forming iodidion. This has been found by experiment to be
e case.

These considerations can be generalised. When in dilute solutions
e solubility of a substance is increased by the addition of another
bstance, this is to be explained by the conversion of the solute into
other compound, to an extent corresponding to the increase of the
lubility, by the substance added. So much passes into solution that
e uncombined portion amounts to about as much as it would do in
e pure solvent; the excess is in a state of combination.

The fact that this rule has been expressed only for dilute solu-
ons is conditioned by the circumstance that larger additions alter
e nature of the solvent and thereby influence the solubility. An
ample of this is to be found just in the case of iodine, which is
ssolved by concentrated solutions of hydriodic acid and of iodides,
much larger quantities than it ought to be according to the above
use alone.

In the brown solutions of iodine in iodides, therefore, only a small
rtion of the iodine can be regarded as existing in the free state,
mely, an amount not greater than is dissolved by water (p. 229).
ill, the solutions mostly behave as if all the iodine dissolved were
ee. This is due to the fact that in proportion as the free iodine is
moved by any reaction, fresh iodine is formed by a splitting up of
e ion I_3' into $I' + I_2$. This process takes place so quickly that there
at no time a complete absence of free iodine so long as any
iodidion, I_3', is still present.

It can be seen that the iodine is indeed combined and not free, by
aking a solution of iodine in carbon disulphide with a large quantity
hydriodic acid or potassium iodide solution. Although no appreci-
le amount of iodine can be removed from this solution by pure water
230), the violet colour in this case for the greater part disappears,
d the iodine passes into the aqueous solution with a brown
lour.

Oxygen Compounds of Iodine.—On dissolving iodine in caustic
la solution, sodium hypoiodite is first formed in accordance with the
ne scheme as in the case of the other halogens. This compound
however, exceedingly unstable, and in a few moments undergoes
unsformation with formation of sodium iodate and sodium iodide.

Hypoiodous acid, therefore, cannot be prepared even in the condition of a dilute solution, but has been observed only in its salts.

From the fact that the solution produced by the action of iodine on caustic soda has different properties at first from what it has later, it follows that something is formed other than the iodide and iodate, which are obtained by crystallisation from the solution. More especially, the freshly prepared solution gives a separation of iodine even with the weakest acids, while later it becomes much more resistant to this action and the iodine separates out much more slowly.

The first stage of the action must, therefore, be formulated thus:—

$$2NaOH + I_2 = NaOI + NaI + H_2O,$$

and the second

$$3NaOI = 2NaI + NaIO_3.$$

The *iodic acid*, from which the salt $NaIO_3$ is derived, is a very stable substance and can be obtained in various ways. Thus, iodine is converted directly into iodic acid, HIO_3, by the action of moist ozone. Other strong oxidising agents likewise form iodic acid from iodine; for this purpose nitric acid is mostly used. The reaction which takes place here cannot be thoroughly understood until later (Chap. XIV.).

The *salts* of iodic acid, or the *iodates*, are formed still more easily. If a solution of potassium chlorate is slightly acidified and warmed with iodine, potassium iodate, iodic acid, and hydrochloric acid are formed—

$$10KClO_3 + 6I_2 + 6H_2O = 10KIO_3 + 2HIO_3 + 10HCl.$$

The iodic acid can be obtained from the liquid by adding a barium salt; difficultly soluble barium iodate then crystallises out and can be decomposed with sulphuric acid. The aqueous solution of iodic acid thus obtained can be evaporated without decomposition.

Iodic acid crystallises from the concentrated aqueous solution in lustrous crystals, which have the composition HIO_3, dissolve readily in water, and impart to this the reactions of a strong acid. In fact, iodic acid is only slightly weaker than the halogen hydracids, which are the strongest known.

On careful heating, iodic acid loses the elements of water and passes into a white, heavy powder, iodine pentoxide—

$$2HIO_3 = I_2O_5 + H_2O.$$

This oxide also dissolves in water, but is thereby transformed a once into the acid, combining again with the elements of water.

If the oxide be still more strongly heated, it decomposes into oxygen and iodine, which is recognised by its violet colour.

If iodic acid and hydriodic acid be brought together, they speedily act on one another, with formation of water and iodine—

$$H^{\cdot}, IO_3' + 5H^{\cdot}, I' = 3H_2O + 3I_2.$$

This reaction does not occur on bringing potassium iodide and iodate together, since the hydrion necessary for the formation of water is wanting. If this, however, be added in the form of some acid, iodine immediately separates out. This reaction can be used as a sensitive indicator for the presence of acid hydrogen, *i.e.* of hydrion. In the case of strong acids or high concentration of hydrion, the reaction proceeds so rapidly that the various steps cannot be followed; with very weak acids, however, it can be seen that the reaction is not complete in a moment, but that it requires time.

Periodic Acid.—If sodium iodate be subjected to the action of specially energetic oxidising agents, it takes up a further combining weight of oxygen and passes into the salt of periodic acid. The periodic acid corresponds to a certain extent to perchloric acid, but differs from it by the fact that in the pure state it is a solid substance, the composition of which is not represented by HIO_4 but by the formula H_5IO_6, containing the elements of two combining weights of water more. On careful heating, periodic acid also loses water and forms an anhydride I_2O_7; whether an intermediate substance of the composition HIO_4 can be obtained has not yet been established.

The behaviour of periodic acid towards bases is different from that of the acids hitherto discussed. Besides the salts of the formula MIO_4, corresponding to the salts of perchloric acid, periodic acid forms salts with three and five combining weights of metal. The formulæ of these are obtained by imagining one or two molecules of water added to the formula HIO_4, and the hydrogen of the compound thus formed replaced by metal. In other words, there exist besides the acid HIO_4, also the acids H_3IO_5 and H_5IO_6. Acids such as these which contain several combining weights of hydrogen replaceable by metals, are called *polybasic* acids. We shall discuss the relations of these acids later, with the help of a simpler and better known example (Chap. XII.).

Chlorides of Iodine.—In the experiment on the decomposition of hydrogen iodide with chlorine described on p. 233, it is observed that if the chlorine is present in excess, the iodine does not separate out in the usual dark lustrous crystals, but that a reddish-brown liquid of the appearance of bromine, and also reddish-yellow crystals, are produced. Both these are new substances formed by the combination of chlorine with iodine.

The red-brown liquid has the composition ICl and is formed with extreme readiness by passing chlorine over iodine. Under the influence of the chlorine, the iodine liquefies, and by starting with weighed quantities the experiment can be interrupted when the increase of weight corresponding to the formula has taken place.

This substance can be solidified by cold, and is obtained in two forms, one of which melts at 14°, the other at 27°. Of these two forms, the one with the higher melting point is stable; the other form, however, is produced more readily by spontaneous solidification when the liquid is cooled down. If a little of the higher melting form be brought into contact with the form of lower melting point, the latter changes into the former; the reverse transformation never takes place. From the liquid cooled below 14°, in the neighbourhood of which temperature the liquid does not spontaneously solidify, the one or the other form separates out, according as crystals of the one or other form are added.

The relations described here are found in the case of a large number of substances. Besides the liquid form, only one kind of which can be present, there are often several solid forms possible, each of which has its special melting point. The form with the lower melting point is always unstable with respect to the form of higher melting point, so that it can pass into the latter, whereas the reverse transformation never occurs.[1] This phenomenon is called *polymorphism*, and the different forms polymorphic forms.

Besides the iodine monochloride, there is another compound, *iodine trichloride*, ICl_3. It is easily obtained by passing an excess of chlorine over iodine; the brown liquid which is first produced soon solidifies to red-yellow crystals, which cannot be melted at ordinary pressure, as they previously decompose into chlorine and vapour of the monochloride. If the decomposition be hindered by an increase of pressure, a melting point under 16 atm. can be observed at 101°.

Both compounds are decomposed by water with formation of hydrochloric acid, iodic acid, and free iodine. Still the trichloride seems to dissolve partially in water without decomposition and to be formed, on mixing concentrated solutions of iodic acid and hydrogen chloride.

Besides these compounds, there exist compounds of iodine and bromine and of iodine and fluorine. These will not be discussed here.

C. *Fluorine*

General.—To the group of halogen elements there must also be added the element fluorine, which differs in its properties more widely from the other three than these from one another. It exhibits, however, still fewer relationships with the rest of the elements, and is, therefore, most suitably classed along with the halogens.

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[1] This holds, in general, only for the behaviour of the substances in the neighbourhood of the melting point. At temperatures which lie at a greater distance below the melting point, the relations can become reversed. An example of this will very shortly be discussed in detail (Chap. XII.).

Fluorine has the combining weight 19, which is smaller than that of the other halogens. The relation which is found here, that the element with the smallest combining weight shows less similarity to the related elements than the elements of higher combining weight to one another, is repeatedly found. Reference will, therefore, be made to this again on other occasions.

Fluorine is not found free in nature any more than the other halogens. To a still higher degree than these, it has the tendency to combine with other elements. This property is so marked that until a few years ago it was quite unknown in the free state.

Compounds of fluorine are fairly widely distributed in nature. It occurs in small quantity in many rocks, and its calcium compound, *fluorspar*, is a very abundant mineral. The total amount of fluorine, however, in the earth's crust accessible to us is considerably less than that of chlorine.

Preparation.—Fluorine is obtained by the electrolysis of its hydrogen acid in exactly the same way as chlorine is obtained by the electrolysis of hydrochloric acid. But in this case the difficulty arises that the aqueous acid cannot be employed for this purpose, since the free fluorine decomposes water with evolution of oxygen and regeneration of hydrogen fluoride. Anhydrous hydrogen fluoride, however, is just as little a conductor of electricity as the other halogen hydracids in the anhydrous state.

The difficulty can be overcome by dissolving potassium fluoride in the anhydrous acid, which thereby becomes a conductor. It is, however, only the hydrofluoric acid that undergoes decomposition, and at the cathode there is obtained hydrogen (primarily and secondarily, cf. p. 195), and at the anode, fluorine.

Since fluorine quickly combines with most of the metals, the electrolysis was first carried out in vessels of platinum, which is not attacked to any considerable extent. It has, however, been since found that copper also resists the attacks of fluorine fairly well, so that the expensive platinum apparatus is not absolutely necessary.

Properties.—Fluorine is a gas with a faint, green-yellow colour, which recalls that of chlorine but is much less strongly developed. Its density is not known with great exactness, but it undoubtedly approximates to the value 38, so that fluorine has the formula F_2, similar to that of the other gaseous elements. Its great reactivity with almost all substances has already been mentioned. In particular, hydrogen compounds of all kinds take fire in fluorine gas, hydrogen fluoride being formed with great development of heat. Most of the metals react violently with formation of fluorides.

The oxygen produced by the action of fluorine on water contains a large quantity of ozone (p. 80). At – 187° fluorine passes into the liquid state.

Hydrogen Fluoride.—Hydrogen fluoride, HF, is obtained, in accordance with the general scheme (p. 205), by the action of other acids on the naturally occurring metal compounds of fluorine, the salts of hydrofluoric acid. As it is readily volatile, it can be separated by warming. In practice, the already mentioned fluor-spar, the calcium salt, and sulphuric acid are employed.

Since hydrofluoric acid has the property of attacking glass, vessels of lead or of platinum must be used in its preparation. For manufacturing purposes the former metal is sufficient, but for scientific purposes the latter must be employed where contamination with lead must be avoided. Fluor-spar and sulphuric acid are mixed and warmed moderately in a retort made of the above material. Hydrofluoric acid distils over, and as the pure acid boils as low as 19°, it can be liquefied by means of an ordinary freezing mixture.

Anhydrous hydrogen fluoride finds no application, but the aqueous solution does. As a rule, therefore, a suitable quantity of water is placed in the receiver in which the hydrogen fluoride can be absorbed, and in this way a solution is obtained, containing 40 to 50 per cent of hydrogen fluoride, which fumes strongly in air. On distillation, hydrofluoric acid behaves exactly like the other halogen hydracids; the constant boiling solution contains 35 per cent of acid and boils at 120°.

The solution cannot be kept in glass vessels, as these are quickly dissolved. Where platinum vessels are too expensive, as in the case of the technical applications, gutta percha is used. This is an organic substance obtained from the lacteal fluid of certain tropical plants, and is very resistant to hydrofluoric acid. Wax, resin, paraffin, and similar substances also resist the acid fairly well, a fact which is of importance for its application.

The use of hydrofluoric acid depends essentially on the fact that it attacks and dissolves glass and similar substances, which contain silicic acid (p. 50). It is used, therefore, on the one hand, for etching glass, and, on the other hand, for the purpose of dissolving compounds of sicilic acid for analysis. The chemical reactions which take place here will be discussed under silicic acid.

* Care must be observed in working with hydrofluoric acid, as its vapour is very injurious, and the acid solution, if it touches the skin, causes painful wounds which heal badly. Washing with ammonia is a remedy for these. The anhydrous acid is especially dangerous. Hydrofluoric acid also acts powerfully on micro-organisms.

By measurements of the electric conductivity of aqueous solutions of hydrofluoric acid, it is found that it is much less dissociated into its ions than the other halogen hydracids. A normal solution, containing one mole in the litre, is rather more than 3 per cent dissociated, whereas the other halogen hydracids are dissociated to 80 per cent. Hydrofluoric acid is, therefore, a considerably weaker acid than the others.

In its general behaviour also, fluoridion differs essentially from the other halogen ions. With silver solutions it gives no precipitate; on the contrary, silver fluoride is readily soluble in water. On the other hand, calcium fluoride is a difficultly soluble substance, whereas the other halogens form extremely soluble compounds with calcium.

The Strength of Acids.—The number of new acids which have just become known to us, gives occasion to some further general considerations in amplification of those made on p. 184. Acids possess a number of common properties which clearly manifest themselves in the colour reactions with litmus and similar colouring substances, and which can also, by means of numerous other reactions, be quantitatively determined.

This similarity in action is appropriately attributed to the presence of the same substance, hydrogen. In the first place, now, we found that the acid properties were by no means exhibited by all hydrogen compounds; all hydrogen, therefore, is not of this nature. The acid hydrogen is characterised chemically by the fact that it can be replaced by metals, as has already been explained on p. 184.

It would, therefore, be expected that those quantities of different acids which contain equal amounts of hydrogen (hence called equivalent), would also exhibit equal acid actions. In certain respects this is the case; thus, such amounts of different acids always neutralise equal amounts of the same base (p. 186), and evolve with metals, *e.g.* magnesium, equal quantities of hydrogen. On the other hand there are other reactions in which the different acids behave differently. For example, on introducing pieces of zinc of equal size into equivalent solutions of hydrochloric acid, sulphuric acid, and acetic acid, the metal acts, it is true, on all the acids with evolution of hydrogen, and the amount of hydrogen which is ultimately evolved is the same in all cases; the *velocity*, however, with which the reaction takes place in the different cases, is very different. It is greatest in the case of hydrochloric acid, less in the case of sulphuric acid, and very small in the case of acetic acid.

* These differences can be clearly shown by placing the acids with the zinc in small flasks fitted with gas-delivery tubes, and collecting the evolved hydrogen in three cylinders of equal section placed side by side and standing over water (Fig. 75). The differences are quite distinct after 5 to 10 minutes if equivalent normal solutions, *i.e.* solutions containing 1·01 gm. hydrogen in the litre, are used. In order to be independent of impurities which may be present in the zinc, and which can cause a difference in the evolution of gas, a small quantity of a dilute solution of copper sulphate is added to each of the solutions.

The evolution thereby becomes rapid and uniform, and the collection of the gas is not begun until somewhat later.

Parallel with these, there run other differences which have reference to the velocity of chemical processes and the equilibrium relations. In all such cases, several of which will be discussed later, the acids are arranged in the same order, so that we must conclude that there are definite differences attaching to the acids themselves and independent of the nature of the reaction.

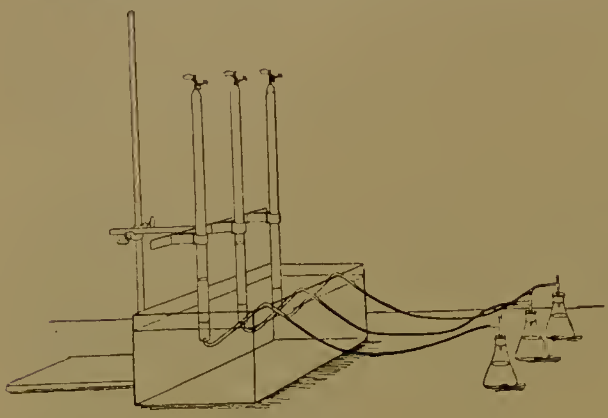

Fig. 75.

Difference in Electrolytic Dissociation.—It has been already mentioned that the acids in aqueous solution are electrolytes, and conduct the electric current with decomposition. If, now, the conductivity of equivalent solutions of the different acids be compared, it is found that in this respect also the acids form the same sequence as in the case of their last mentioned properties. Hydrochloric acid conducts best, sulphuric acid less well, and acetic acid much worse. Agreement is found in every detail, and is present also in the numerical values. It follows from this that we are dealing with the operation of the same cause and any interpretation of the described relations must take account of all these properties.

The power of conducting the electric current was attributed (p. 197) to a special condition of the participating substances, the ionic condition. In this condition the components exist in a certain degree of independence of one another, or of freedom, and this finds its expression just in the power of transporting opposite electricities in opposite directions.

The same independence is proved by the identity of the chemical reactions of an ion, independently of the presence of other ions (p. 189).

The great differences in electrical conductivity of equivalent solutions of acids, and the corresponding differences in chemical reactivity, are to be attributed to the fact that *not the whole amount but only a portion of the acid present is in a state of free ions.* By this portion alone the electric conduction is performed, and on it depend the velocity and the equilibrium in the case of the reactions of the acids. Of the whole hydrogen of an acid, then, a portion is present in the state of ions, while the other portion is combined with the anion. Only the hydrogen which is present in the ionic condition determines the velocity of the action of the acids on zinc, the different chemical equilibria, and (in conjunction with the anion) the electrical conductivity.

For this reason, all these different actions are found to vary in a similar manner with the nature of the acid, and to be proportional to one another.

* The great differences in electrical conductivity can be made very clear by placing the solutions in narrow tubes and passing an electric current through them and through a galvanometer which indicates milliamperes (Fig. 76). A fairly high potential must be used in order to lessen, as far as possible, the influence of the secondary potentials which make their appearance at the electrodes, and which are due to reactions taking place there. It is best to make the connection with the electric main, which has usually a potential of 60 to 110 volts, although five or ten accumulators arranged in series, corresponding to 10 or 20 volts, are sufficient. Under these conditions the deflection of the instrument is proportional to the electrolytic conductivity. In the case of equivalent normal solutions of the three acids mentioned, the ratio of the conductivities is found to be about 1 : 0·5 : 0·012.

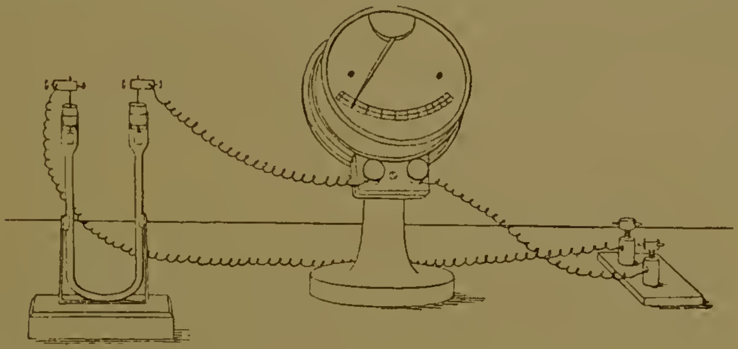

FIG. 76.

* The suitable dimensions of the tubes are found from the rule that with a length of 10 cm. the section must amount to $\frac{1}{\sqrt{n}}$ cm., where n is the potential in volts used, in order that normal hydrochloric acid shall allow a current of about 100 milliamperes to pass. If the tubes are increased in length, the section must also be proportionately enlarged.

The process by which the acids which in the pure state are not electrolytes split up on solution into ions, is called electrolytic dissociation (p. 197). Different acids undergo this dissociation to different extents, and the greater the degree of dissociation, the more pronounced are the acid characters, the "*stronger*" is the acid. The strength, however, cannot increase indefinitely, for it must reach its maximum when dissociation is complete.

As a matter of fact, measurements of the conductivity have shown that there is a maximum for the strength of acids which cannot be exceeded. Hydrochloric acid, even in moderately dilute solutions, approximates to this maximum, and must, therefore, be designated as one of the strongest acids. To the same class belong the other halogen acids, with the exception of hydrofluoric acid, which is considerably less dissociated.

The dissociation of hydrochloric, hydrobromic, and hydriodic acids, as well as that of all other acids, increases with the dilution. In the following table there is given the fractional dissociation at the ordinary temperature (20°), the dilution being expressed by the number of litres in which 1·01 gm. of hydrogen is contained.

Dilution.	HCl.	HBr.	HI.	HF.	Sulphuric Acid.	Acetic Acid.
10	0·95	0·95	0·95	0·10	0·57	0·013
100	0·98	0·98	0·98	0·26	0·74	0·050
1000	0·99	0·99	0·99	0·59	0·92	0·125

Whereas, therefore, the first three acids change only slightly with the dilution, the others do so to a large extent, and tend to assume the value 1—a value which is already almost reached by the former. The more dilute the acids, the more nearly do they approach one another in strength.

These relations obey certain laws which we shall not consider, however, until a later point.

When we speak, therefore, of the strength of an acid, we mean its dissociation, *i.e.* the fraction of the total amount which is in the form of ions. The conception applies, naturally, only to aqueous solutions. The strength varies also with the temperature and the dilution, but although the absolute values of the degree of dissociation are thereby altered, the *order* of the different acids remains unchanged.

* An approximate measure of the strength of an acid is afforded by the comparison of its conductivity with that of an equivalent solution of hydrochloric acid. Since at fairly great dilution, the latter does not materially fall short of complete dissociation, the conductivity of the acid referred to hydrochloric acid equal to unity, gives the fraction of its hydrogen which is in the ionic condition, or the degree of dissociation of the acid. We have here, it is true, neglected certain conditions, still these cannot give rise to any considerable errors.

Of the oxy-acids of the halogens, chloric, bromic, iodic and perchloric acids are dissociated to approximately the same extent as hydrochloric acid. Hypochlorous acid, on the other hand, is very slightly dissociated; the exact degree of dissociation, however, is unknown.

Actual and Potential Ions.—Since hydrion has just been designated as the substance which manifests the typical acid reactions, and it has further been shown that in solutions of acetic acid of moderate concentration only 1 to 2 per cent of the hydrogen is present in the ionic form, one might suppose that on titrating with caustic soda the red colour of the litmus would disappear after this hydrion had been converted to water by the addition of a few per cent of the equivalent of alkali. This is not the case. On the contrary, we have seen that the different acids require exactly as much alkali as corresponds to their equivalent (p. 186). For the process of neutralisation, therefore, it is a question not merely of the hydrion but of *all* the acid hydrogen, whether it is present as ion or not.

This apparent contradiction is removed when we consider more carefully what is the course of the process of neutralisation. On addition of caustic soda, the ions $H^{\cdot}$ and OH' in the first place act on one another and form water. There exists, however, a chemical equilibrium which depends on the proportions of the participating substances, between the portion of the acid which has passed into ions and the undissociated portion. If one of the substances is removed, that reaction must immediately take place by which it is again replaced. In proportion, therefore, as the hydrion is removed by combination with the hydroxidion, a fresh amount must be produced by the dissociation of the still undissociated portion. This new formation can take place as long as there is undissociated acid present, but when this is used up the hydroxidion will no longer be bound, and the blue colour of litmus must appear.

Now, all processes between ions proceed, as experience shows, so quickly that it has hitherto never been possible to measure their velocity. In the case of our experiment, therefore, we see only the final result, and on titration with caustic soda we do not obtain the amount of hydrion present at the particular moment, but the amount of *all* the hydrion that can be formed from the substances present; not the *actual* amount of the ions, but *the sum of the actual and the potential.*

The same holds for the action of the metals, *e.g.* zinc, on the acids, where the total amount of the possible hydrion is ultimately evolved as hydrogen gas. In this case, however, the *velocity* is measurable, and it is found to be all the greater, the greater the concentration of the hydrion actually present. The same is found in all processes which depend on the hydrion and which proceed with measurable velocity.

The question as to the conditions under which only the actual, and under which the potential ions are to be considered, can be answered to the effect that the former are all-important when the amount of the ions present is unaltered, or is altered only in an incomparably slight degree, by the process. If, however, the process is of such a nature that ions are removed by it, and that it continues as long as ions of the particular kind are present, it will depend on the total amount of all possible ions. By means of this rule each separate case can be decided.

Thus, the precipitation of chloridion by silver solution is, evidently, a process which gives the amount of the *potential* ion. When the silver is present in sufficient amount, the process does not cease until all the chloridion, not only that present at the beginning, is exhausted. For the chloridion is removed from the solution by the precipitation of the silver chloride in the solid state, and the process can continue so long as chloridion can still be formed from the undissociated chloride present.

The determination of the electrical conductivity, however, gives information only as to the amount of the *ions really present* or the *actual* ions, for by such a measurement no ions, or only a vanishingly small amount of ions, are used up.

From this it is clear that in order to measure the state of dissociation or, generally, the concentration of any ions, only those processes are directly applicable by which the amount of the ions is not, or is only very slightly, altered.

The Dissociation of Salts.—Whereas in the case of the acids, and, as we shall find later, to a certain extent also in the case of the bases, great variety exists in the degree of dissociation,—all possible values, in fact, occurring,—the behaviour of the neutral salts is much more uniform. Almost all these are dissociated to a fairly large extent and only in quite exceptional cases are salts found which exhibit deviations in this respect.

Except in these special cases, therefore, it will not be necessary in the case of chemical reactions between salt solutions to refer specially to the state of dissociation. The actual conditions will be represented very closely if we assume that all the salt present is dissociated into its ions, and that the reactions take place exclusively between the ions.

An important conclusion which can be drawn from this is that when different salt solutions are mixed with one another, the liquid thus produced will always be of the same nature, if it contain the same ions in the same amount, no matter what the arrangement of these ions was in the salts used for the preparation of the solution. A mixture of equivalent amounts of sodium chloride and potassium iodide can in no respect be distinguished from one prepared from the corresponding amounts of potassium chloride and sodium iodide.

Further, since the state of the substances present is not altered by mixing the two solutions—for the substances were present as ions to start with and are so also after the mixing—none of those processes take place by which the occurrence of chemical change is characterised. There occurs no change either of the temperature or of the volume or of the colour, etc., and the properties of the mixed solution are simply the sum (rightly formed) of the properties of the components of the mixture.

Where a deviation from these rules is found, it is a proof that the assumption made is no longer correct, but that there can be formed from the ions present one or several salts which are dissociated to a much less degree into ions.

Again, new conditions arise when a salt can be formed which separates out in the solid state under the existing conditions. Since the solid salts are not dissociated, those phenomena which accompany a chemical process must forthwith appear, *i.e.* there is development or absorption of heat, and all the other properties also undergo a sudden change.

* These relations can be made clear by mixing solutions of sodium chloride and potassium iodide previously brought to the same temperature. No change of temperature is indicated even by a very sensitive thermometer. So soon, however, as one of the salts is chosen so that a precipitate can be formed (*e.g.* potassium iodide and lead nitrate, or sodium sulphate and barium chloride), an appreciable rise of temperature occurs on mixing.

* **Hydrolysis.**—In the case of the salts of weak acids a special phenomenon is met with, the comprehension of which rests on the theory of strong and weak acids. On testing a solution of sodium hypochlorite (p. 204), for example, with litmus paper, it is not found to be neutral, like sodium chloride or a similar salt, but the solution is distinctly alkaline. This is a peculiarity met with in the case of many other salts of weak acids, and the explanation of it is as follows.

A weak acid is one in which the dissociation into hydrion and the corresponding anion is slight. When, therefore, the two kinds of ion come together, they will for the most part combine until one of them has almost disappeared.

If, now, we have an aqueous solution of the sodium salt of a very weak acid, the anion of the acid is present in large amount. In this case, a very small quantity of hydrion is sufficient to establish the equilibrium; and if more hydrion is present, the greater part of it will combine with the anion until its amount has so far diminished that the condition of equilibrium can exist.

In the aqueous solution, now, hydrion is present because water is dissociated, although only slightly still in measurable amount, into the ions hydrion and hydroxidion (p. 191). This small concentration is greater than corresponds to the equilibrium with the ion ClO'. Hydrion, therefore, will unite with this to form undissociated $HClO$. By this process, however, the equilibrium between the ions of water is disturbed, further amounts of water must dissociate into hydrion and hydroxidion, and these processes will go on till all the substances are in equilibrium.

The result of these processes is the disappearance of a certain quantity of hydrion which has been used for the formation of $HClO$. The corresponding amount of hydroxidion cannot unite with the sodion, because sodium hydroxide is a strongly dissociated electrolyte, but remains in the free state. A solution, however, which contains hydroxidion reacts alkaline, and this, indeed, is what the solution of sodium hypochlorite does.

At the same time a certain amount of the undissociated compound HClO has been formed, and this, we know, is volatile (p. 206). The solution must, therefore, smell of hypochlorous acid. This also is a general peculiarity of the hypochlorites.

The above considerations will, evidently, preserve their validity in all cases where we are dealing with salts of strong bases and weak acids. The phenomenon is known as *hydrolysis*, since it is a case of decomposition with the co-operation of water, and the general rule can be stated that *hydrolysis will always occur when the salt of a weak acid with a strong base is dissolved in water.* The behaviour of the solution, also, can be characterised by saying that the acid and the base have not neutralised one another completely, so that the reactions both of the base and of the free acid can be observed side by side.

Similar considerations also apply to the salts of weak bases. These are also hydrolytically dissociated and, for a corresponding reason, react acid. At a later point we shall have an opportunity of returning to this.

Hydrolytic dissociation differs essentially from electrolytic dissociation (p. 197). The latter occurs in the case of all salts, and especially in the case of those of the strong acids and bases; but hydrolysis is possible only when the acid or base, or both, are weak, *i.e.* slightly dissociated in solution.

General Remarks on the Halogens.—The four elements fluorine, chlorine, bromine, and iodine form a natural family of similar elements, whose properties, in the widest sense of the term, generally follow the same order as the combining weights. In the first place, the numerical values of these fundamental magnitudes exhibit a definite relation to one another. On placing them together and taking the differences, we obtain the following:—

		Difference.
Fluorine . .	19	16·45
Chlorine . .	35·45	44·51
Bromine . .	79·96	46·89
Iodine . .	126·85	

The differences between chlorine, bromine, and iodine are almost equal, but the difference between fluorine and chlorine shows a marked deviation.

In accordance with this, the elements chlorine, bromine, and iodine form a group of more closely related elements, from which fluorine, in its whole behaviour, is comparatively far removed.

The physical properties of the free elements form the same regular series as the combining weights. Fluorine is a gas which is difficult to liquefy, chlorine can be easily liquefied, bromine is liquid under ordinary conditions, and iodine is solid. The density of the elements in the liquid state and, as may be at once added, the densities of corresponding compounds in the liquid or solid state, also stand in the same order.

All halogens form acids with one combining weight of hydrogen. Of these, that of fluorine is medium strong, while those of the other halogens are very strong. The heat of formation of the dilute acid decreases regularly as the combining weight increases, and in the same way the difference of energy between the free element and the corresponding ion diminishes; the tendency to ion formation is very great in the case of fluorine, but in the case of iodine it has already become very slight. The lighter halogen, therefore, always displaces the heavier from its salts, *i.e.* the lighter halogen passes into the ion form and the heavier into the elementary state.

With the metals, also, the halogens form compounds which possess similar composition. Thus, if a chloride, say, contains two combining weights of chlorine, the same number is found in the case of the bromide, the iodide, and the fluoride. This follows at once from the composition of the acids, which, on account of their containing the same number of combining weights of hydrogen, are able to neutralise the same quantities of the different bases.

In their behaviour towards oxygen, the order of the halogens is reversed. Fluorine gives, so far as known, no compound with oxygen; the oxygen compounds of chlorine can be prepared, but have slight stability, likewise, also, the bromine compounds; and the iodine compounds are the most stable. In this case, it is true, we do not have such complete regularity as in the other cases, for the compounds of bromine are less stable than those of chlorine; in this respect, therefore, chlorine stands between bromine and iodine, instead of bromine being between chlorine and iodine.

With regard to these irregularities, however, we should remember that the relations we have just mentioned depend on the temperature, and alter to an unequal extent when this is changed. It is, therefore, very possible that at other temperatures, the usual order would again obtain, and that this apparent irregularity is only the outcome of a farther reaching regularity which at present escapes our judgment.

The relation we have met with here, that the elements can be arranged in groups of similar substances, will be frequently found again. In all these cases the law is repeated that the properties of such elements and of their corresponding compounds can be arranged in the same way, so that the numerical values of the combining weights are found to be the basis of the systematic treatment of the properties both of the elements and of their compounds.

It is true, however, that on attempting to introduce numerical relations in place of the mere order of arrangement, we encounter great difficulties. The chief cause of these is that the properties undergo alteration to varying degrees with varying conditions (*e.g.* with change of temperature), so that the relations which exist under certain conditions become different when we pass to other conditions. Simple numerical relations can exist only in those cases where the magnitudes are unaffected by any condition (as, for example, in the case of the law of the combining weights), or where the influence of the conditions is the same in all comparable cases (as in the case of the law of gaseous volumes). In all other cases numerical relations which shall at the same time be *exact* and simple, cannot be expected, and if they are observed in any one case, it will, in general, be a mere chance.

Thermochemistry of the Halogens.—In accordance with the example given in the case of chlorine (p. 199), the thermochemical relations of the other halogens can be investigated. The following table gives a clear summary of the determinations and calculations.

Heat of Formation.	Fluorine.	Chlorine.	Bromine.	Iodine.
Hydracid, gaseous	161 *kj*	92 *kj*	35 *kj*	−26 *kj*
,, dissolved in water	205	164	118	+55
Oxy-acid HAO, in solution	—	125	109	—
,, HAO_3 ,,	—	100	51	234
,, HAO_4 ,,	—	161	—	199

In the above calculations, the elements are assumed to be in the state in which they exist at room temperature, viz. chlorine gaseous, bromine liquid, iodine solid. The existing differences are not greatly altered by recalculating the numbers to the gaseous state.

Heat of Neutralisation with Caustic Soda.	Fluorine.	Chlorine.	Bromine.	Iodine.
Hydracid	68 *kj*	57 *kj*	57 *kj*	57 *kj*
Oxy-acid HAO	—	42	42	—
,, HAO_3	—	58	58	58
,, HAO_4	—	59	—	—

(All the substances are dissolved in much water.)

A consideration of the above numbers shows that the behaviour of the corresponding halogen compounds is somewhat different in the three groups. Whereas the heat of formation of the hydracids, both in the gaseous state and in aqueous solution, shows a marked decrease from fluorine to iodine, the heat of formation of the oxygen compounds of iodine is in all cases greater than that of the corresponding chlorine compounds. Bromine, however, does not stand in the middle, but its numbers are smaller than those of chlorine and iodine.

Another picture is presented by the heats of neutralisation of the halogen hydracids. Whereas these are equal for hydrochloric, hydrobromic, and hydriodic acids, hydrofluoric acid has a considerably higher value. The equality of the numbers in the case of the former acids is due to the fact that these are to a large extent dissociated into ions in the dilute aqueous solutions used; the heat of neutralisation is, therefore, equal to the heat of formation of water from its ions hydrion and hydroxidion, as was shown on p. 200. The greater heat of neutralisation in the case of hydrofluoric acid is connected with its slight dissociation in aqueous solution (p. 200), and, indeed, it can be concluded that the dissociation of hydrofluoric acid into its ions takes place with *evolution* of heat. For we can regard the neutralisation of this acid by caustic soda as if the acid first dissociated into ions and the hydrion then combined with the hydroxidion of the soda to form water, while the fluoridion and the sodion remain side by side in the solution, in accordance with the circumstance that sodium fluoride, being a neutral salt, is, in aqueous solution, dissociated to a large extent into ions (p. 246). The total heat evolution consists, therefore, of the heat of dissociation of the hydrofluoric acid and of the heat of formation of water from hydrion and hydroxidion. The latter reaction gives a heat development of 57 *kj*; the excess, 68 − 57 = 11 *kj*, is, therefore, the heat developed in the dissociation of hydrofluoric acid into ions.[1]

On comparing the heats of formation of the halogen hydracids with the known chemical reactions which occur between these and the free halogens, it is found that there take place between them those reactions which are accompanied by an evolution of heat. Thus, chlorine displaces bromine and iodine from their hydrogen compounds, and, in aqueous solution, an amount of heat equal to 164 − 118 = 46 *kj* and 164 − 55 = 109 *kj* is set free. Very nearly the same evolution of heat is found in the case of the salts of the halogens, because the heats of neutralisation of the three acids with most bases are equal, and their influence is, therefore, cancelled.

* Similar relations can be frequently observed, and have given rise to the idea that one can predict the direction of the corresponding chemical reaction from the sign of the "heat effect," by which term there is understood both the development and the absorption of heat. Such a theorem would contain the assumption that only those chemical reactions can take place which develop heat.

* Now, although, as a matter of fact, the majority of the known chemical reactions take place with development of heat, there are not a few known in which the opposite, the absorption of heat, occurs, so that the temperature of the reacting substances falls spontaneously. The attempts to attribute the absorption of heat in such cases to secondary reactions or to changes of the physical state, have failed, for the difference between primary and secondary reactions is just as arbitrary as that between physical and chemical changes of state. On

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[1] Since the hydrofluoric acid is somewhat dissociated, and also the sodium fluoride contains some undissociated salt, this number does not give the whole amount for a mole, but only a part. This circumstance changes somewhat the numerical value of the result, but not its general character.

the contrary, the conclusion was unavoidable that such a theorem cannot be established, since it is in contradiction to the facts.

* If we recall the statements made on p. 208, we see that it is the difference of the *free energy* that determines a chemical reaction. The differences of the heats of formation, however, are a measure not of the changes of the *free* but of the *total* energy. For this reason, direct conclusions cannot be drawn from the one set of figures with regard to the other set.

* So far, however, as determinations have been possible, the differences between the free and the total energy are, in general, not great. One may conclude, therefore, with a certain degree of probability, that in those cases where the differences of the total energy are large, the corresponding differences of the free energy will have, if not the same value, at least the same sign. With this reservation, it will certainly be possible to draw conclusions as to the direction of the reaction from the sign of the heat of the reaction. In all cases, however, in which the heat of reaction is small, the conclusion becomes doubtful.

* One case in which a reaction takes place spontaneously with absorption of heat, can be at once discussed on the basis of the table on p. 250. On adding a solution of hydrochloric acid to a solution of sodium fluoride an absorption of heat of 10 *kj* occurs. This is due to the fact that in this case the ions of hydrofluoric acid, fluoridion, and hydrion come together. Hydrofluoric acid, now, is slightly dissociated in solution; its ions, therefore, must combine whenever they come together. This combination, however, is accompanied by an *absorption* of heat, for the dissociation of hydrofluoric acid into its ions, as we have just seen, develops heat. Since the other ions, viz. chloridion and sodion, remain unchanged in the experiment, no other causes of a heat effect exist, and the reaction takes place, as observation shows, with absorption of heat.

* Since in this reaction undissociated hydrofluoric acid is chiefly formed, the process was formerly interpreted as if the "weaker hydrofluoric acid is displaced from its compound with sodium by the stronger hydrochloric acid." As the above consideration shows, the impelling cause lies not so much in the hydrochloric acid as in the hydrofluoric acid, the slight dissociation of which conditions the reaction. This can, it is true, take place only in the presence of a "strong" acid, for such an acid is one that is to a large extent dissociated into its ions, and only such an one, therefore, can yield the requisite amount of hydrion.

CHAPTER XII

SULPHUR AND ITS COMPOUNDS

A. *Sulphur*

General.—The solid, yellow, easily fusible and combustible substance well known by the name of sulphur, is an element in almost the pure state. It occurs fairly widely distributed in nature in the form of elongated octahedral crystals of a honey-yellow colour. The occurrence of sulphur is especially connected with volcanic phenomena. The whole consumption of sulphur in Europe has for a long time been supplied by Sicily. At the present day large quantities of free sulphur are also obtained from compounds of sulphur which are exceedingly abundant in nature.

Forms of Sulphur.—The sulphur of commerce has the appearance of slightly conical rods, the form of which is due to the fact that the liquid sulphur has been poured into wooden moulds and allowed to cool. If a stick of sulphur be broken, cavities are frequently found in the interior lined with crystals. These have a different appearance from the naturally occurring sulphur, for they exhibit oblique, prismatic forms which have no similarity to the octahedra of the native sulphur. On closer examination, however, they are found to be *pseudomorphs, i.e.* crystals having only the external shape but not the inner character of this crystalline form.

The fact is that sulphur is capable of existing in several different solid forms. If it be allowed to crystallise at temperatures of 100° or over, it forms the oblique prisms mentioned above. If, however, it crystallises at low temperatures it appears in the same octahedral forms as the naturally occurring sulphur.

Crystallisation from the Fused Mass. — These phenomena can be readily observed by melting a fairly large quantity of sulphur, say 1 kilogm., by gentle heating; fusion takes place at 120°. If the liquid be now allowed to cool, the temperature falls most rapidly at the sides of the vessel and at the surface. In these regions crystals are formed and grow inwards into the central, liquid portion. If, after a short time, the surface crust of solid sulphur be broken and the liquid portion poured out, the crystals which have been formed will be exposed and a large number of them will be found on breaking the mass of sulphur.

For a short time after they have been formed, these crystals are of an amber-yellow colour and can be bent slightly without breaking. On the following day, the appearance of the crystals has considerably changed; they have assumed the lemon-yellow colour of the ordinary roll sulphur and have become brittle.

Crystallisation from Solution.—If, on the other hand, sulphur be dissolved in a suitable solvent, the best being carbon disulphide (p. 230), and the liquid be allowed to evaporate, crystalline sulphur also separates out. This, however, has the octahedral forms of natural sulphur and undergoes no change on being kept at room temperature.

If, however, the octahedral sulphur (natural or artificial) be heated to temperatures of over 100°, without being melted, it also becomes cloudy and brittle.

The Regions of Stability.—The above phenomena are due to the fact that to each of the two forms of sulphur there corresponds a range of temperature in which the one form is stable, but in which the other form is unstable and is converted into the former. The range of the octahedral sulphur extends from low temperatures up to 96°, that of the prismatic sulphur from 96° to 120°, its melting point. Below 96°, prismatic sulphur is unstable and passes into octahedral; above 96°, octahedral sulphur is unstable and passes into prismatic.

These relations show a very great similarity to the reciprocal transformation of ice and water, or, generally, to fusion and solidification. As in those cases so also in the present, there is a temperature above which only the one form, and below which only the other form, is stable. On passing this point, therefore, the one form passes into the other, and only at this one temperature can the two forms exist together.

Influence of Pressure on the Point of Transition.—Considering that we are dealing here with a single substance we shall expect, in accordance with the phase law (p. 171), that there will be only one temperature and one definite pressure at which three phases can exist side by side. At 96°, these phases are octahedral sulphur, prismatic sulphur, and sulphur vapour. If we exclude the vapour, the presence of which determines a definite, very small pressure, the temperature of equilibrium of the two forms of sulphur varies with the pressure. The temperature of transition, indeed, is raised by pressure, because the prismatic sulphur occupies a larger volume than the octahedral. However, as in the case of ice and water (p. 129), a very great pressure is here necessary in order to effect a slight shifting of the temperature of equilibrium. For the rest, the two forms of sulphur behave as two independent substances. Not only the crystal line forms, but also the density, the power of refracting light, the melting point and all other properties, are different. The density of prismatic sulphur is 1·96, that of octahedral, 2·07.

The prismatic crystals obtained from the fused sulphur, and which have become opaque, have the density 2·07, the density of the octahedral form. This is the simplest proof that they have really become converted into octahedral sulphur. We have the reverse phenomenon in the case of the octahedral sulphur transformed by heating.

Suspended Transformation. — Just as water can be cooled below 0° without solidifying to ice, the temperature of transformation of the two forms of sulphur can be overstepped from both sides. If octahedral sulphur be rapidly heated, it melts at 115°, which is its true melting point. If, however, it be slowly heated, so that it has time to undergo transformation, fusion is observed at 120°, the melting point of prismatic sulphur.

Enantiotropy and Monotropy.—A comparison of the behaviour of the two forms of sulphur here described with the two chlorides of iodine (p. 238), reveals an essential difference. Whereas in the case of the chlorides of iodine, only the one form is stable and the other is unstable, in the case of sulphur, both forms are stable, each one being stable in its own range of temperature and unstable in the range of temperature of the other.

The difference lies in the fact that in the case of sulphur, the melting point of the more readily fusible form is above the temperature of transition at which the stability of the two forms changes, whereas in the case of the chlorides of iodine, the less stable form melts before the temperature of transition is reached.

Substances like iodine monochloride, which can undergo transformation only in one direction, are called *monotropic*, and those which, like sulphur, can change in both directions, *enantiotropic*.

Other Forms of Sulphur.—Other crystalline forms of sulphur, differing from the two already described in form and in other properties, can be obtained by strongly heating small quantities of sulphur and allowing it to cool rapidly. They are, however, all unstable with reference to the octahedral and prismatic sulphur, and, according to the temperature, pass into the one or other of these. In respect of these forms, therefore, sulphur is monotropic.

We need not here describe these forms in greater detail, as they are only of rare occurrence and have only a passing existence.

Sulphur has also been known for a long time in the form of *flowers of sulphur* and *milk of sulphur*. These two kinds of sulphur are not special forms in the scientific sense, but represent only peculiar states of division of sulphur and consist chiefly of octahedral sulphur, at least after being kept some time.

Flowers of sulphur is produced in the distillation to which sulphur is subjected for the purpose of purification (p. 260). So long as the condensing chamber is cold, the vapours on falling down solidify in small crystals, and sulphur is obtained in the form of a yellow powder which has been known from the time of the alchemists as flowers of sulphur. The powder almost always contains, however, small quantities of amorphous sulphur.

By the name *milk of sulphur* there is denoted a very finely divided form of sulphur which is precipitated from aqueous solutions in certain reactions. These processes will be described later. In this way sulphur is obtained in such a fine powder that its yellow colour becomes almost invisible and it emits almost entirely white surface light (p. 13). On account of its finer state of division and correspondingly large surface, this form of sulphur more readily undergoes chemical change; on this fact depends the application of milk of sulphur in medicine. Milk of sulphur does not differ chemically from ordinary sulphur.

Liquid Sulphur.—We return now to the properties of sulphur. As already mentioned, prismatic sulphur melts at 120°; it thereby changes into a light yellow, mobile liquid which, on cooling, solidifies at once to prismatic sulphur. In small drops, however, and by excluding particles of solid sulphur, liquid sulphur can be strongly supercooled. It then exhibits properties quite similar to those of supercooled water.

If the melted sulphur be further heated, it exhibits very remarkabl phenomena. Whereas, in general with rise of temperature, the internal friction of liquids decreases, we find the opposite behaviour in the case of liquid sulphur. The higher the temperature rises, the more viscid does it become. At the same time it becomes darker in colour, and at 250° it passes into a dark red mass, which is so viscous tha the vessel may be turned upside down without it running out. O further heating, the mass again becomes more liquid, without, however losing its dark colour. At 450° the sulphur is again quite liquid an boils, passing into a red-brown vapour.

The heated sulphur, on being allowed to cool, again passes throug all these conditions in the reverse order; it first becomes viscid, the liquid again and light in colour, and solidifies, finally, in prismati crystals.

Amorphous Sulphur.—Strongly heated sulphur behaves quit differently on being rapidly cooled, as *e.g.* by pouring it into col water. It then assumes a viscid character like that of elastic or indi rubber, and is called *amorphous* sulphur.

This designation denotes that the sulphur in this form is n crystalline, although it exhibits, to a certain extent, the properties of solid body. On the other hand, it can be regarded as a liquid wit great internal friction. This view is supported by the fact that amo phous, solid substances, on heating, exhibit a *continuous* transition int the liquid state; no definite melting point can be observed, but the internal friction continuously decreases. All the other properties also change continuously, until a state with the characteristic properties of a liquid is produced.

Transformations.—The amorphous, viscid sulphur does not remain in this condition at ordinary temperatures. After some days, sometimes also only after a fairly long time, it changes into an opaque, brittle mass which, from its density, proves to be octahedral sulphur.

We must conclude from this that at ordinary temperatures, the amorphous sulphur is a less stable form than the octahedral. As a matter of fact, the latter is the only form of sulphur which is stable at room temperature; all the other forms, of which there are several besides those already mentioned, pass in course of time into octahedral sulphur. This is, accordingly, the only form which is found in nature.

The fact that the rapidly cooled sulphur does not immediately pass into that form which is stable at the existing temperature, but that it first assumes a less stable form, is a special case of the general law that when changes of state take place those forms are usually produced which are the least stable of the forms possible under the existing conditions (p. 207). The forms first produced afterwards change into the more stable ones, when this becomes possible. The velocity of this transformation varies greatly, and the transformation may take place in the fraction of a second or may last for years or centuries. The changes in the properties of liquid sulphur with the temperature which have been described, lead to the conclusion that sulphur, in the liquid as in the solid state, can assume different allotropic forms. It has hitherto not been possible to prepare these forms in the pure state and to characterise them.

* **Experiments.**—On account of the variety of its forms, sulphur is specially well adapted for a study of the reciprocal relations and conditions of stability of different forms of the same substance. These relations can be observed in a very instructive manner by melting a small piece of sulphur in a tube about 2 cm. wide, exhausting the tube, and sealing it off.

On slightly heating the spot where the sulphur is situated, the latter gives off vapour, and on the colder parts of the tube drops (not crystals) of sulphur are deposited, although the temperature is there much below the point of solidification of sulphur. The less stable, liquid form, therefore, is first produced.

If the tube be allowed to remain in this state for some hours and the deposit of drops be examined with a lens, the following appearance is found. Many of the drops still remain liquid, as can be seen from their transparency; others have solidified to crystals. Where a crystal has formed, it is quickly encircled by a clear ring, the surrounding drops disappearing. This is due to the fact that the vapour pressure of the crystallised sulphur is smaller than that of the liquid at the same temperature. For the crystalline form is the more stable of the two, and must, in accordance with the considerations put forward on p. 132, also have the smaller vapour pressure. Sulphur distils, therefore, from the drops to the crystals, and the former disappear from the neighbourhood.

Occasionally, also, other regions are seen in the tube where no crystal has formed, but where, nevertheless, the formation of a "halo" is found. On closer examination of such a spot, it is seen that the centre of the clear space is occupied by a drop which is larger than those surrounding it. In accordance with the reasoning just applied, we must conclude that larger drops of sulphur have a smaller vapour pressure than small ones. This also is the case, and follows from perfectly similar considerations.

Thus, on bringing two drops into contact, they unite with a certain force and form a single drop. This union takes place in consequence of the surface tension of the liquids, by virtue of which a liquid tends to assume that shape which has the smallest possible free surface. In the case of large masses of liquid, the surface tension is small compared with the influence of gravity; in the case of small quantities of liquid, however, it is the determining factor and is the cause of the spherical shape of the drops.

Now, the surface of the sphere formed by the fusion of two drops is smaller than the sum of the two spherical surfaces before the union. Since the surface tension tends to diminish the surface, there exists also the tendency to form a large drop from several small ones. This tendency exerts itself in all ways in which the object can be attained. Since it can also be attained by distillation, the cause of the distillation, viz. the difference of the vapour pressure, must be such that this tendency is given effect to. The vapour pressure of small drops, therefore, must be greater than that of large drops, as experiment also shows.

If the tube with the deposits of liquid and solid sulphur at various parts be allowed to remain undisturbed for a fairly long time, the deposits all disappear, and there is only the large piece of sulphur seen in the tube, which has now become clear. All the sulphur has, therefore, distilled over to the large piece. The cause is the same as before; for solid substances also have a surface tension, and, therefore, there exists the tendency to make the surface as small as possible or the pieces as large as possible.

For the *solubility*, exactly the same considerations hold as for the vapour pressure. If a glass plate, such as is used as an object glass for microscopic purposes, be held over heated sulphur until a deposit has been formed on it, and if a drop of water (or of glycerine, to avoid evaporation) be placed on this and the whole covered with a cover-glass, exactly the same phenomena of "halo" formation and the consumption of the less stable forms by the more stable are observed. This experiment serves at the same time to demonstrate the solubility of sulphur in these liquids, a solubility that is so small that it has not been possible in any other way to observe or to measure it.

Applying these considerations to the conditions of transformation of the octahedral and prismatic sulphur, we can draw the following conclusions. The solubility of the former in any solvent must, below 96°, be smaller, and, above 96°, be greater, than that of the prismatic. Consequently, the solubility at 96°, the point of transition, must be the same for both forms. All this has been confirmed by experiment.

Since the considerations on which these conclusions are based are general, the law can be enunciated for all allotropic forms that the less stable forms must be more soluble than the more stable, and that at the point of transition the solubility of the two must be equal. Useful application of this law can be made in cases where the transformations are difficult to observe.

Sulphur Vapour.—A similar variety of conditions is shown by sulphur in the vaporous, as in the solid and liquid form. At temperatures in the neighbourhood of the boiling point, the molar weight of sulphur vapour is 220; the higher the temperature is raised, the smaller does the molar weight become, until at 1000° it has fallen to 64, and at still higher temperatures it retains this value. These numbers are for atmospheric pressure. If the vapour of sulphur is investigated under smaller pressures, it is found that at a given temperature the molar weight is all the smaller the lower the pressure. This variability also ceases when the molar weight reaches the value 64. Sulphur vapour, therefore, follows neither the law of Boyle nor that of Gay Lussac, and only when the molar weight has become equal to 64 does it behave in accordance with these laws.

A similar behaviour has already been met with in the case of iodine (p. 231), and the same interpretation of the phenomena can be applied in this case, *i.e.* the vapour of sulphur exists in several forms with different molecular weights. Since the combining weight of sulphur is 32, the formula S_2 must be ascribed to the vapour which is stable at the high temperature and low pressure. With regard to the more dense form, the present case is more difficult than that of iodine, in so far as no region is known in which the density is constant. Even at the boiling point of sulphur we are in the region of variable vapour density. Since the highest observed value of the density amounts to 230, we can only conclude that the denser vapour contains more than six combining weights, or that in its formula S_n, n is at least greater than 6.

From determinations of the molar weight of *dissolved* sulphur in different solvents (cf. p. 156), the formula S_8 has been found for it. It can therefore be assumed with some degree of probability that the denser sulphur vapour also has the formula S_8, and that the vapour of variable density consists of a mixture of S_2 and S_8. The possibility that other kinds of sulphur vapour S_n, where n is a whole number between 8 and 2, are present, is pretty well excluded by recent experiments.

With reference to the law set forth on p. 231, it follows as a necessity that on diminishing the pressure the less dense form of the vapour S_2 should be formed at the expense of the more dense S_8. From the fact also that this transformation is brought about by elevation of temperature, it can be concluded that the transformation from S_8 to S_2 takes place with absorption of heat.

Purification of Sulphur.—Use is made of the changes of state which sulphur undergoes, for the purpose of purifying it. As found in nature, it is usually mixed with other minerals, clay, and sand. In Sicily, the sulphur ore is piled up in a heap furnished with air channels, like the wood pile for the burning of charcoal, and is set fire to. The heat produced causes the sulphur to melt, and this flows away in a fairly pure condition, leaving the difficultly fusible impurities behind. By this method a loss of sulphur is incurred, owing to the combustion of a portion of it, but this is by far the cheapest means of generating the heat necessary for the melting of the sulphur.

To completely free the already fairly pure sulphur so obtained from all non-volatile impurities, it is *distilled* from iron retorts, and the vapours are led into large chambers of mason work. At the commencement of the distillation these chambers are cold, and the sulphur vapours condense to a fine powder of sulphur particles. These are, at first, amorphous (cf. p. 256), but soon pass for the greater part into the crystalline condition. The powder is in part collected and is placed on the market under the name of *flowers of sulphur* (p. 255). On continuing the distillation the temperature of the chamber rises above 120°, and the sulphur then collects in it in the liquid state.

The liquid sulphur can be run off through an opening at the bottom of the chamber. It is collected in wooden moulds, in which it solidifies in rods of a slightly conical shape known as *roll sulphur*.

* B. *Crystals*

General.—The two known forms of solid sulphur differ not only in density and other properties, but also very materially in the form of their crystals, and the general question arises, therefore, as to the laws of crystalline form. All the more importance attaches to this question from the fact that the crystalline form is a property of almost all solid substances, and constitutes a very important means of describing and identifying these.

In the first place we draw the distinction between the two conditions of solid substances, the *amorphous* or formless, and the *crystalline* or formed. Since, however, the outward shape can be changed at will, some other more general characteristic must be sought for by means of which the two conditions can be distinguished.

The essential nature of crystalline bodies is found in the fact that their properties vary in a manner depending on the *direction in space.* For example, a ball of glass and one of octahedral sulphur, on being warmed, will behave differently. Whereas the glass ball remains a sphere, only increasing somewhat in size, the ball of sulphur passes, on being warmed, into an ellipsoid, the axes of which have a simple relation to the shape of the crystal from which the ball was cut.

Another example is furnished by the conduction of heat. If a glass plate be covered with a layer of wax and the point of a hot metal cone be placed on this, the wax is melted in the form of a circle, because the heat is distributed equally quickly in all directions. If the same experiment be carried out with plates cut from crystals, the melting takes place not in circles but in ellipses whose axes have different relative lengths according to the position of the plate in the original crystal, and likewise stand in a definite relation to the shape of the crystal.

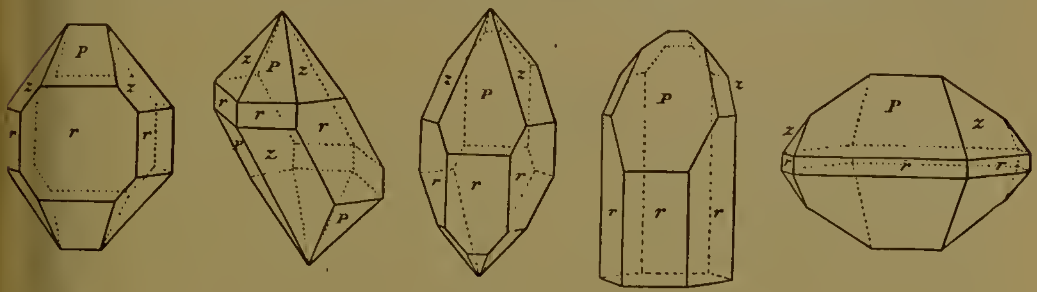

FIG. 77.

The Crystalline Forms.—By the name *crystal*, one is accustomed to think, in the first instance, of the regular forms which substances assume on passing into the solid state, and which can so often be observed in such exquisite beauty in the case of naturally formed solid bodies. The examples discussed teach that these forms are merely a definite expression of a much more comprehensive regularity. The forms are only an expression of the general fact that in crystals all properties which can be brought into relation with the direction in space undergo regular variation with this direction. Of the properties which concern us here, the most important is certainly the external shape, since it is, on the one hand, the one which first forces itself on the observation, and, on the other hand, exhibits the most manifold variety to be met with in the case of crystals.

Crystalline forms have the general property that they are bounded only by plane surfaces. If one examine, however, a group of simultaneously formed crystals of the same substance, *e.g.* a cluster of quartz crystals, it is soon seen that the appearance of the individual crystals is very varied, the outlines of the bounding planes being quite different. All the same, these various crystals (Fig. 77) preserve a certain relationship of form, which at once forces itself on one's notice.

Closer investigation shows that although the outline and the size of the faces which bound the crystals change, it is always possible to so place the different crystals that to every face of the one there stands a face of the other parallel to it. From this it follows that the angles at which the various corresponding faces of two crystals meet, are always the same. Owing to one or other of the faces being formed relatively near or relatively far from the middle point of the crystal, the faces cut one another differently, but the angles between them remain the same.

Further, a cursory examination shows that the crystals are *symmetrical* structures. By this there is understood that different faces occur in a crystal, which are similar to one another and are repeated in a regular manner. Thus, for example, the snow crystals figured on p. 116 have the property that each may be regarded as consisting of three similar parts arranged round the centre at angular distances of 120°.

The Symmetry of Crystals.—All the regularities exhibited by crystals can be deduced on the basis of the conception of symmetry.

Three kinds of symmetry are to be distinguished. The first is that which exists between an object and its mirror-image; the plane of the mirror is called the plane of symmetry of the structure.

A second kind of symmetry arises by rotating an object round a definite axis through an angle equal to a simple fraction of the total rotation, and repeating the rotation until the object again reaches its original position. According as this angle is $\frac{1}{2}$, $\frac{1}{3}$rd, $\frac{1}{4}$th, or $\frac{1}{6}$th of the total rotation, we speak of a binary, ternary, quaternary, or senary axis of symmetry. (Other grades, such as quinquenary, septenary, or higher, are not possible in crystals.)

The third kind of symmetry arises from a combination of the two just described, by *rotation and reflection*. If the object is brought into its next position by a rotation followed by a reflection, so that by repeating this process a number of times it again comes into its original position, such a structure possesses the third kind of symmetry. For our studies, it is essentially the first two kinds of symmetry, reflection and rotation, that are of account.

By using the three kinds of symmetry, or two or one of them, and by combining them in every possible way, thirty-two different cases are obtained.

All the crystals which occur correspond to one of these cases, so that by the application of the principle of symmetry a complete system of all possible crystalline forms is obtained.

The Seven Systems of Crystals.—Into all these cases, however, we cannot enter, but must content ourselves with the characterisation of seven of the larger groups.

Crystals possessing no element of symmetry are called *triclinic*. The simplest form of this is the oblique angled parallelopiped (Fig. 78).

Crystals with *one plane of symmetry* are called *monoclinic.* The simplest form is the parallelopiped with four rectangular and two oblique angled faces (Fig. 79).

Crystals with two planes of symmetry perpendicular[1] to one another are called *rhombic.* Their simplest form is a rectangular parallelopiped (Fig. 80).

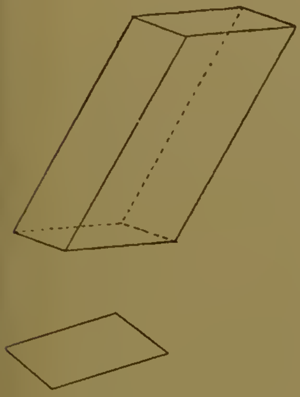

FIG. 78.

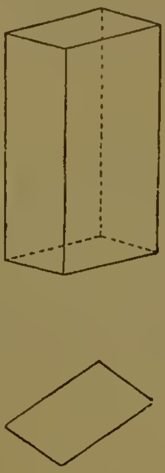

FIG. 79.

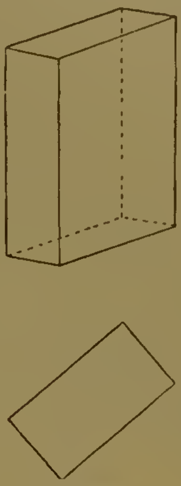

FIG. 80.

Crystals with a quaternary axis of symmetry are called *quadratic.* The simplest form is a rectangular parallelopiped with quadratic base (Fig. 81).

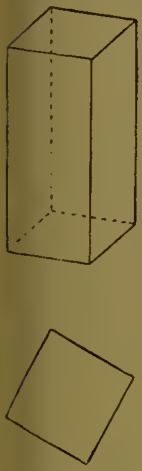

FIG. 81.

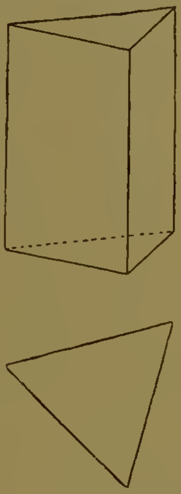

FIG. 82.

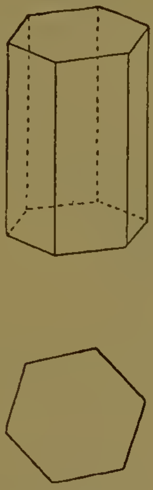

FIG. 83.

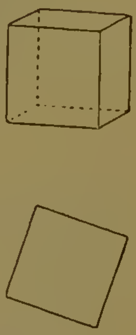

FIG. 84.

Crystals with a ternary axis of symmetry are called *trigonal.* The simplest form is a three-sided right prism (Fig. 82).

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[1] When two planes of symmetry are not at right angles to one another, a third plane of symmetry is required by the reflection of the one in the other, and by the reflection of this third, a fourth, etc. If, therefore, more than two planes of symmetry, which cut in a straight line, are to be excluded, they must be perpendicular to one another.

Crystals with a senary axis of rotation are called *hexagonal*. The simplest form is the six-sided right prism (Fig. 83).

Crystals with three binary axes of symmetry perpendicular to one another and also equivalent are called *regular*. By equivalent is meant that the crystal always presents the same shape when it is turned so that its axes of symmetry assume positions previously occupied by other axes of symmetry. The simplest form of the regular crystals is the cube (Fig. 84).

Derived Forms.—Besides the simplest forms just mentioned, there are many others derivable from them geometrically, which obey the laws of symmetry valid for the particular kind of crystal.

The possibilities which arise are, however, so numerous that they cannot be treated here. We shall, however, state a law which renders their mutual connection clear.

Imagine a large number of small crystals of one of the simplest forms mentioned above, and all of the same size, to be given. By arranging these in a regular manner, other forms can be built up. From a number of small cubes, for example, the form shown in Fig. 85, which is known as an octahedron, can be built up. It is only necessary to imagine new planes laid through the corners of the cubes, touching these corners, or, what amounts to the same thing, one imagines the cubes to be so small that the unevenness caused by the re-entrant corners can no longer be noticed.

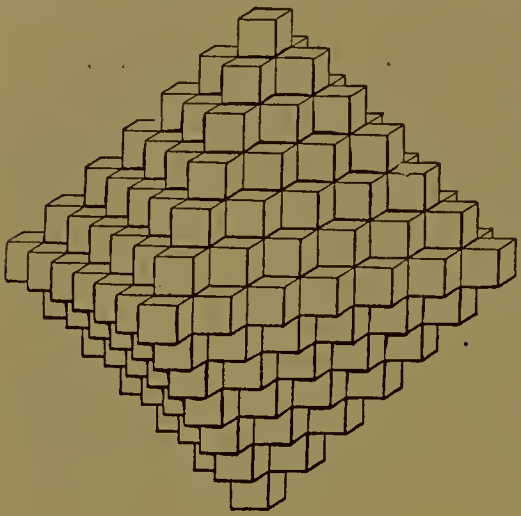
Fig. 85.

The law in question states that *all forms occurring in different crystals of a substance, can be built up in the manner described from small crystals of the simplest form, the conditions of symmetry being at the same time observed.*

The law stated here can be expressed mathematically in various ways. What we have said will be sufficient to show that the crystalline form of a given substance can be characterised by the statement of the simplest form.

The Other Properties of Crystals.—As has already been mentioned on p. 261, all the properties of crystals which can in any way become dependent on the direction in space, have a regular orientation. The question arises, therefore, whether any connection exists between the external shape of the crystals and the orientation of the other properties.

The answer is that such a connection certainly exists. It can be stated thus: *The symmetry in the arrangement of the other properties is always found again in the symmetry relations of the external form.*

Let us take, as an example, a chemical phenomenon which readily occurs in the case of hydrated crystals, viz. *efflorescence.* This consists in the water evaporating at different points of the crystal, a compound containing less water, which can be distinguished from the main portion by its different colour, remaining behind as a powder. If the efflorescence is allowed to take place with such precautions as to avoid the formation of detached spots, it can be established that the regions of efflorescence have, in the most general case, the form of spheres or ellipsoids.[1] Further, it is possible, from the shape of the crystal, to predict what the form of the efflorescence figure will be.

If the crystal is regular, the efflorescence figure is always a sphere, for in regular crystals there are three planes of symmetry perpendicular to one another and equivalent. Of the shapes mentioned as occurring, the sphere and the ellipsoid, the sphere is the only one through which three equivalent perpendicular planes of symmetry can be laid.

The crystals of the trigonal, quadratic, and hexagonal systems have one axis of symmetry in which three, four, or six planes of symmetry lie. An ellipsoid which can be divided in this way must be a *monoaxial* one, *i.e.* an ellipsoid produced by the rotation of an ellipse about one of its axes. This axis of rotation must coincide with the axis of symmetry of the crystal, since it is only in this way that the ellipsoid can be divided by the corresponding planes of symmetry into from three to six identical portions.

It is not possible, however, to distinguish tri-, tetra-, or hexagonal crystals by the difference of the ellipsoids of efflorescence. For a monoaxial ellipsoid may contain any number whatever of planes of symmetry laid through its axes of rotation. It makes no difference, therefore, whether there are three, four, or six.

Besides the monoaxial ellipsoid, there is the triaxial. It is produced by the rotation of an ellipse about one of its axes, the other axis being lengthened or shortened during the rotation, so that its ends (and at the same time also all other points of the ellipse) describe not circles but ellipses. Such a form has three planes of symmetry, which are determined by the axes of the generating ellipses, and are perpendicular to one another.

The same symmetry relations are also met with in the case of the rhombic crystals. It is to be expected, therefore, that the efflorescence forms of the rhombic crystals will be represented by triaxial ellipsoids, the planes of symmetry of which coincide with those of the crystalline form. This conclusion is confirmed in every case by experience.

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[1] Of course only parts of these forms can be observed, viz., their intersections with the faces on which the spots occur. By observing the spots on different faces of the same crystal, however, the whole efflorescence figure can be constructed.

In the case of monoclinic crystals, only one plane of symmetry exists. Only one of the three planes of symmetry of the ellipsoid, therefore, can be determined by the crystalline form, and the two others are indeterminate, *i.e.* they lie in a manner which is dependent on the nature of the crystal but not on its form.

In the case of triclinic crystals there is no plane of symmetry. The ellipsoid of efflorescence is, therefore, entirely independent of the shape.

Generalisation.—What has just been stated for efflorescence, holds also for many other properties of crystals, viz., for all those whose arrangement in the crystal can, in the most general case, be represented by a triaxial ellipsoid. Under this definition come the transmission of light, of heat, of electricity, the changes of form by pressure on all sides, and still other properties. The most important of these is the transmission of light, for the optical properties of crystals have been subjected to a thorough scientific investigation, and are used for the identification of the crystalline system in those cases where the external shape gives no information or no complete information. It can be stated generally, that every optical phenomenon in a crystal is subject to the symmetry relations explained above, and that from the observation of the nature of the symmetry of any optical phenomenon whatever, a conclusion can be be drawn as to the crystalline system, within the limits stated.

C. *Sulphuretted Hydrogen*

The Compounds of Sulphur.—Sulphur is capable of forming compounds with almost all elements, in some cases in very different proportions. More especially, all metals form with sulphur compounds which have generally a similar composition to the corresponding oxygen compounds, and which are called *sulphides*. Many of these occur abundantly in nature and form sources for obtaining the metals and also sulphur.

Further, sulphur forms a number of acids with hydrogen and oxygen, the chief of these being sulphuric acid. The salts of this acid, the sulphates, also occur widely distributed in nature, and find a manifold application in the arts and in medicine.

To convince oneself of the power of sulphur to enter into combination, the following experiments may be performed. Heated in the air, sulphur burns with a blue flame, forming an oxygen compound with a choking smell, sulphur dioxide. A mixture of sulphur and iron powder in the proportion of 4 parts to 7, becomes incandescent on being slightly heated, the sulphur combining with the iron to form a black, slag-like mass of *iron sulphide*. If sulphur be heated to boiling in a test-tube and strips of thin copper-foil be introduced into the vapour, the copper becomes incandescent and combines with the sulphur, also forming a black compound. Metallic mercury combines with sulphur even at room temperature. If 1 part of sulphur be rubbed together with 6 parts of mercury in a mortar, combination takes place with formation of mercury sulphide of a deep black colour. Likewise, silver combines with sulphur even at ordinary temperatures; silver coins and other objects of silver rapidly become black in a pocket in which sulphur matches have lain, the small quantities of sulphur present combining with the silver.

Sulphuretted Hydrogen.—Similarly to chlorine, bromine, and iodine, sulphur can combine with hydrogen to form an acid, which is called hydrogen sulphide or sulphuretted hydrogen. At ordinary temperatures it is gaseous, but can be condensed by pressure and cold to a liquid which boils, under atmospheric pressure, at – 64°.

The molar weight of sulphuretted hydrogen is 34; it contains 32 parts of sulphur to 2 parts of hydrogen. Since the combining weight of sulphur is 32, the formula of sulphuretted hydrogen is H_2S. Unlike the halogen hydracids, sulphuretted hydrogen contains *two* combining weights of hydrogen replaceable by metals, and in consequence of this there is an essential difference in the combining power of this acid.

Dibasic Acids.—If we consider what compounds can be formed when the hydrogen of the sulphuretted hydrogen is replaced by metals, *e.g.* sodium, we find there are *two* different salts conceivable, according as only *one* combining weight or *both* combining weights of hydrogen are replaced by metal. Expressed in formulæ, we should expect the compounds, NaHS and Na_2S. As a matter of fact, both compounds are known.

To distinguish it from the acids which contain only one combining weight of replaceable hydrogen, which can, therefore, react with only one combining weight of a base to form a salt, and which are called monobasic acids, sulphuretted hydrogen is called a *dibasic* acid. Generally, a dibasic acid is one which contains in a mole, two combining weights of replaceable hydrogen.

The salts of dibasic acids in which both hydrogens are replaced by metals, are called *neutral* or *normal* salts. Salts which contain only one combining weight of metal along with one hydrogen, and which, therefore, still contain the characteristic component of acids, hydrogen, are called *acid* salts.

The former are also called *secondary* and the latter *primary*. Further, they are designated by using the Greek numerals mono-, and di-, which refer to the number of combining weights of metal (not of hydrogen) present; monosodium sulphide is the salt NaHS, disodium sulphide, Na_2S. Finally, compounds containing the group HS are called *hydrosulphides;* NaHS is sodium hydrosulphide. All these terms are in use side by side.

The Ions of Dibasic Acids.—Whereas monobasic acids can dissociate into ions in only one way, two different reactions are possible in the case of the dibasic acids, yielding two different kinds of anions. The dissociation occurs, in the first place, according to the equation

$$H_2A = H^{\cdot} + HA',$$

where A is the divalent anion of the acid. That is to say, a monovalent anion HA′ is formed along with hydrion. This process corresponds exactly to the ordinary electrolytic dissociation of the monobasic acids.

A new reaction, however, then occurs, viz.:—

$$HA' = H^{\cdot} + A'',$$

the monovalent anion undergoing a further dissociation into hydrion and the divalent anion A″. The reaction

$$H_2A = 2H^{\cdot} + A'',$$

which might be regarded as that directly taking place, can be conceived of as the result of two processes occurring one after the other.

The aqueous solutions of such acids, therefore, always contain two kinds of anions, and the different acids are distinguished by the extent to which the one or other process takes place.

The dissociation of a dibasic acid into its ions always begins with the first reaction. If the acid is not very strong, this process greatly predominates, and the second stage of the dissociation takes place only in a slight degree. In other words, such acids behave exactly like monobasic acids, dissociating into hydrion and a monovalent anion.

On the other hand, if the acid is very strong, the ion HA′ further dissociates into H˙ and A″, and the solution will principally contain this divalent ion.

The solution of an acid salt of a *weak* dibasic acid, having the formula MHA, forms the ions M˙ and HA′, and as the latter possesses the power of dissociation only in a slight degree, only a small part of the ions HA′ dissociate further into A″ and H˙. The acid salt, therefore, has only a slight acid reaction, and behaves approximately like a neutral salt.

If, however, we have a salt of a *strong* dibasic acid, the ions M˙ and HA′ are, it is true, first formed, but the latter undergoes further dissociation into the ions H˙ and A″. The solution of such a salt contains the ions A″, M˙, and H˙. Hydrion, therefore, is present in comparatively large amount, and the solution behaves principally like the solution of an acid.

An example of the first case is afforded by sulphuretted hydrogen; we shall soon find in sulphuric acid an example of the second.

* On dissolving the neutral salt M_2A, the ions 2M˙ and A″ are directly formed, and in the case of strong acids the matter rests there.

In the case, however, of a dibasic acid in which the second dissociation is only slight, a reverse action appears. Since the ion AH' is much more stable than the ion A'', there is a tendency for the former to be produced at the expense of the latter. The hydrion which is present in small amount through the dissociation of the water, is drawn upon to form this ion according to the equation $A'' + H^{\cdot} = HA'$. Hydrion is thereby used up, and the corresponding amount of hydroxidion remains over. This is a process very similar to that of the hydrolysis of the salts of weak monobasic acids (p. 247), the effect of which is also that an excess of hydroxidion is finally present. The solution, therefore, acquires an alkaline reaction; it turns red litmus paper blue, and phenolphthalein red.

The Salts of Sulphuretted Hydrogen.—The above difference can be very clearly observed in the case of sulphuretted hydrogen. The "acid" salts, *e.g.* $NaHS$, in aqueous solution, behave neutral to litmus; the normal salts, *e.g.* Na_2S, however, react strongly alkaline. This is due to the fact that HS' behaves as an extremely weak acid. In the solution of the sodium salt $NaHS$, the ion present, HS', is so slightly dissociated that the reaction of the hydrion, the reddening of litmus, is not visible. In the solution of the normal salt, hydrolysis (*vide supra*) occurs to a large extent, according to the equation

$$Na_2S + H_2O = NaHS + NaOH,$$

or, taking account only of the reaction of the ions,

$$S'' + H_2O = HS' + OH'.$$

The hydroxidion formed is the cause of the turning blue of red litmus, or, in general, of the alkaline reaction.

* The relations described here are very frequently found, and vary only with the relative strength of the dibasic acids with respect to their two hydrogen ions. More especially is hydrolysis of the normal salts of very frequent occurrence in the case of dibasic acids of medium strength. Hence arises the contradiction that the salts, which, on account of both hydrogens present being replaced by metals, are called *neutral* salts, do not react neutral but alkaline. It is preferable, therefore, to use the term *normal* salts, or one of the other names given on p. 267.

Preparation.—Sulphuretted hydrogen is obtained by the decomposition of its salts, the metallic sulphides, by stronger acids. Thus, it can be obtained from the two sodium salts of sulphuretted hydrogen by means of hydrochloric acid, according to the equations

$$Na_2S + 2HCl = 2NaCl + H_2S,$$
$$NaHS + HCl = NaCl + H_2S.$$

As can be seen from the second equation, the acid salt is the more economical for the preparation of sulphuretted hydrogen, since for the same amount of salt only half the amount of hydrochloric acid is required.

On account, however, of its cheapness, iron sulphide is generally used instead of sodium sulphide for the preparation of sulphuretted hydrogen. We have already got to know this substance as the product of the interaction between sulphur and iron (p. 266); it is also prepared on the large scale in a similar manner. Under the influence of hydrochloric acid the following reaction takes place:—

$$FeS + 2HCl = FeCl_2 + H_2S.$$

The iron sulphide consists of equal combining weights of iron and sulphur; the symbol Fe denotes iron. On comparing the formula of this compound with that of sulphuretted hydrogen, H_2S, it is seen that one combining weight of iron has taken the place of two combining weights of hydrogen. Such metals are called *divalent*, whereas metals which, like sodium, can replace only one combining weight of hydrogen, are called *monovalent*. Trivalent and polyvalent metals are also known.

Sulphuretted hydrogen is prepared and used in large quantities in the laboratory on account of its action on metallic salts, which will be presently mentioned. For its preparation on a comparatively small scale, the apparatus described on p. 86 can be used, iron sulphide, in large pieces, being introduced into the lower part and decomposed with hydrochloric or sulphuric acid. Where, however, larger quantities of sulphuretted hydrogen are regularly required, the apparatus shown in Fig. 86 will be found serviceable.

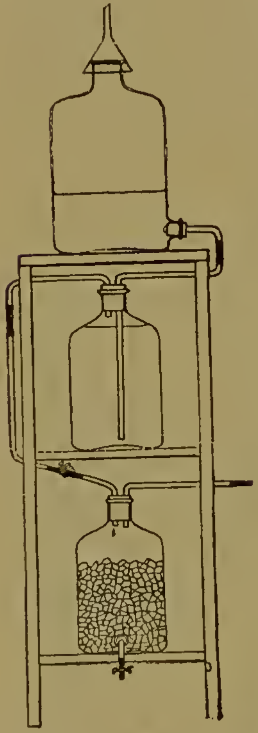
FIG. 86

This consists of three bottles with tubulures at the bottom, placed one above the other. From the top bottle a tube passes to the bottom of the middle one, and from the neck of this a tube, carrying a pinch-cock, passes to the lowest bottle, which is filled with iron sulphide. The sulphuretted hydrogen is led away through a short tube, also fitted with a cock, which passes through the doubly-bored cork of the lowest bottle.

If the top bottle be filled with dilute hydrochloric acid and the two cocks opened, the acid first flows into the middle bottle, and from this it passes in drops, by suitable regulation of the cock, to the iron sulphide in the lowest bottle. The sulphuretted hydrogen is here evolved, and can be led off through the second tube to be used as required. When no more gas is required, the delivery tube is closed. The acid ceases to flow into the lowest bottle on account of the excess of pressure. The sulphuretted hydrogen produced by the small amount of acid which is still in the lowest bottle, collects in the middle bottle, the acid being forced into the uppermost bottle. The apparatus is now in readiness to supply any quantity of sulphuretted hydrogen at any moment.

As compared with the Kipp apparatus, this one has the advantage that the full effect of the acid is obtained, whereas in the case of the Kipp apparatus the fresh acid is mixed with the partially spent, its action thereby becoming slow and incomplete.

When the acid in the top bottle is used up, fresh acid is filled in, and the neutral solution of the iron salt contained in the lowest is run off through the bottom tubulure. One charge of iron sulphide suffices for many fillings of acid.

Properties.—Sulphuretted hydrogen has an extremely unpleasant smell of rotten eggs, or rather rotten eggs smell of sulphuretted hydrogen, this gas being given off by the albumin, which contains sulphur, in the process of putrefaction. It is a rather powerful poison for higher organisms. Certain low organisms, however, can live in the presence of sulphuretted hydrogen, as can be seen from the fact that the process of putrefaction in which the gas is formed is a chemical process brought about by micro-organisms. Sulphuretted hydrogen dissolves in water, imparting to this its smell and a feeble acid reaction. The solubility is not very great. One volume of water absorbs 4·4 volumes of the gas at 0°, 3·7 volumes at 10°, and 3·1 volumes at 20°. At atmospheric pressure and room temperature a solution is obtained containing 1 mole in about 12 litres.

The Solubility of Gases.—In most of the cases already discussed of the absorption of gases by water, chemical changes of the solute occurred along with the process of solution, so that the process was not seen in its simplicity. In the case of sulphuretted hydrogen the chemical phenomena recede to such an extent that the pure process of solution remains almost uninterfered with.

The greater the pressure under which a gas stands, the more of it dissolves in a liquid, the *amount dissolved being, indeed, proportional to the pressure.* This law was discovered by Henry in 1803, and is called after him.

Since the amount of a gas which is contained in a given space is also proportional to the pressure, the law of Henry can be stated in another form, viz., *a liquid always dissolves the same volume of a given gas, independent of the pressure.*

This form of the law allows of a simple definition of the solubility of a gas. This may be defined as the volume of the gas absorbed by the unit of volume of the liquid, and we obtain, in this way, a number which is independent of the pressure.

Moreover, the solubility depends also on the temperature, becoming, as a rule, smaller as the temperature rises. This is connected with the fact that in the absorption of gases, heat is in most cases developed (p. 130).

For example, the solubility of oxygen and hydrogen in water is small; it amounts to 0·01 – 0·03, *i.e.* one litre of water dissolves only from 10 to 30 cc. of these gases, according to the temperature, so that this solubility can for many purposes be neglected. In the case of these gases, the law of Henry holds with the same degree of approximation as the general gas laws. The more soluble the gases are in water, the greater are the deviations from the law of Henry. In the case of sulphuretted hydrogen, the solubility of which at room temperature is as much as 3, the law, however, still holds. Deviations of importance do not occur until the solubility exceeds 100.

* **Relation to the Law of Distribution.**—On comparing this law with the law of distribution stated on p. 230, a large measure of agreement is found. The law of Henry can also be stated in the form, that the ratio of the concentrations in the gas and in the solution has a constant value. For the concentration in the gas, or the ratio of the amount to the volume, is proportional to the pressure, and since the amount dissolved is also proportional to the pressure, it follows that this new form of the law is correct. In this way the gas space becomes comparable with a solvent or a solvent with a gas space. We shall soon see that we are dealing here with more than an external similarity.

It can also be easily seen that the law of distribution is a consequence of the law of Henry. If we imagine two mutually immiscible liquids simultaneously brought into equilibrium with a gas or vapour, each of the liquids must, in the first place, absorb an amount of the gas proportional to the pressure. If p is the pressure and a_1 and a_2 the amount of the gas absorbed by the solvent S_1 and S_2 respectively under the unit of pressure, the amounts absorbed under the pressure p are pa_1 and pa_2 respectively. If the pressure is now changed to P, these amounts are Pa_1 and Pa_2. In both cases the ratio is $a_1 : a_2$, independent of the pressure.

We now make use of the theorem that what is in equilibrium in one way is in equilibrium in every way (p. 132). Let us imagine the solutions to be prepared not by the saturation of each of the solvents with the gas, but by absorbing the gas in one liquid and shaking this with the other. In this case also, equilibrium can occur only when the gas is distributed between the two in such a way that the concentrations are in the ratio $a_1 : a_2$. This, however, is the law of distribution.

Since, finally, in applying the law of Henry there is no limit on the side of small pressures, the above reasoning can be applied to all substances, however small their vapour pressure. But to all substances there may, after all, be ascribed a finite, although often an immeasurably small, vapour pressure, so that the law of distribution has to be regarded as valid for all substances. This is also found by experiment to be the case (p. 230).

The assumption, however, must remain fulfilled that the substance which is distributed undergoes no chemical change in one of the solvents. In such a case the law of distribution no longer holds (p. 230); but the law of Henry also loses its validity (p. 271). In this also the close connection between the two laws is seen.

The Strength of Sulphuretted Hydrogen.—Sulphuretted hydrogen is not a strong acid. It can be readily removed from its aqueous solution by boiling or by means of an exhaust pump, a thing which cannot be done in the case of the solutions of the strong gaseous acids, such as hydrochloric acid. Its salts, also, are readily decomposed by other acids, as is evident from the description of its preparation.

The determination of the electrical conductivity of aqueous solutions of sulphuretted hydrogen yields very small values, from which it may be concluded that only quite a small part of the substance has passed into ions, the greater portion being present as undissociated sulphuretted hydrogen. When, therefore, disulphidion and hydrion come together in solution, they at once combine, with the exception of quite a small residue, to form undissociated sulphuretted hydrogen, and if the concentration of this is greater than corresponds to the solubility under atmospheric pressure, the gas must escape in the form of bubbles.

As a matter of fact, in the evolution of the gas from sodium sulphide in solution and hydrochloric acid, the following process must be assumed:—

$$Na^{\cdot}_2S'' + 2H^{\cdot}Cl' = 2Na^{\cdot}Cl' + H_2S,$$

or, since on both sides the sodion and chloridion remain unchanged,

$$S'' + 2H^{\cdot} = H_2S.$$

Theory of the Evolution of Sulphuretted Hydrogen from Iron Sulphide.—How are we, now, to view the evolution of the gas from hydrochloric acid and *iron* sulphide, since the latter is generally regarded as insoluble? The answer is that the iron sulphide is *not* insoluble, although it is only very slightly soluble. The solubility, however, is sufficient for the formation of disulphidion in the solution along with diferrion. Then the reaction

$$S'' + 2H^{\cdot} = H_2S$$

takes place, more iron sulphide dissolves, and these processes are repeated so long as iron sulphide and hydrochloric acid are present. Only when the concentration of the hydrion has become very small and that of the diferrion very large, is a chemical equilibrium established, and the evolution of sulphuretted hydrogen ceases.

As is evident from this explanation, the possibility of generating sulphuretted hydrogen from difficultly soluble metallic sulphides, depends essentially on the solubility of these. As a matter of fact, all readily soluble metallic sulphides, without exception, give the reaction. Of the metallic sulphides which are apparently insoluble,—in reality, however, only difficultly soluble,—some are readily decomposed by hydrochloric acid, *e.g.* manganese sulphide, iron sulphide, zinc sulphide; these are the most readily soluble of the difficultly soluble sulphides. Other sulphides, such as copper sulphide, silver sulphide, and mercury sulphide, are so slightly soluble that the process described takes place only to an inappreciably small extent. These metallic sulphides are not decomposed, but can remain unchanged in the presence of acids.

Analytical Reactions of Sulphuretted Hydrogen.—On the same relations depends the application of sulphuretted hydrogen in analytical chemistry. Such a process as

$$FeCl_2 + H_2S = FeS + 2HCl,$$

i.e. the decomposition of ferrous chloride by sulphuretted hydrogen, with formation of iron sulphide and hydrochloric acid, cannot take place in aqueous solution, because the reverse action between hydrochloric acid and iron sulphide takes place, with formation of ferrous chloride and sulphuretted hydrogen. The corresponding reaction can, however, take place with mercury—

$$HgCl_2 + H_2S = HgS + 2HCl,$$

for mercury sulphide is not decomposed by hydrochloric acid. If, therefore, we have a solution containing iron and mercury salts, the mercury can be precipitated as almost insoluble mercury sulphide by passing in sulphuretted hydrogen gas. The iron salt remains unchanged in the solution, and in this way a separation of the two salts can be effected.

Many other metals behave in an exactly similar manner. Further, since the sulphur compounds generally have a conspicuous colour,—white, yellow, red, brown, or black,—it is often possible to tell what metals are present merely from the appearance of the precipitate. On this behaviour depends the application of sulphuretted hydrogen for analytical purposes; the details will be given when describing the different metals.

In accordance with the equation given on p. 273,

$$S'' + 2H^{\cdot} = H_2S,$$

the decomposition of metallic sulphides of the nature of iron sulphide by acids, depends on the action of hydrion present. If hydrion is not present, the difficult solubility of iron sulphide comes into evidence when diferrion and disulphidion come together in solution, that compound being formed according to the equation

$$Fe^{\cdot\cdot} + S'' = FeS.$$

This occurs, for example, when a solution of sodium sulphide is mixed with one of ferrous chloride—

$$Na_2^{\cdot}S'' + Fe^{\cdot\cdot}\ Cl'_2 = FeS + 2Na^{\cdot}Cl'.$$

For this reason a black precipitate of iron sulphide is obtained under these conditions.

Those difficultly soluble metallic sulphides which are not precipitated from acid solution by sulphuretted hydrogen, can be precipitated from a neutral solution by sodium sulphide, or similar readily soluble sulphides. This behaviour is also made use of in analytical chemistry.

Sulphuretted Hydrogen as a Reducing Agent.—If exposed to the air, a solution of aqueous sulphuretted hydrogen soon becomes turbid and deposits a white precipitate. The liquid which remains is pure water. The process consists in the oxidation of the sulphuretted hydrogen by the oxygen of the air—

$$2H_2S + O_2 = 2H_2O + 2S.$$

The sulphur separates out in a state of very fine division, and has, therefore, the white colour of milk of sulphur (p. 256).

By reason of this power of combining with oxygen, sulphuretted hydrogen acts as a reducing agent, and it is occasionally used for the purpose of removing oxygen. Similarly, hydrogen compounds can be prepared with the help of sulphuretted hydrogen.

Preparation of Hydrogen Iodide.—If, for example, sulphuretted hydrogen be passed into water in presence of iodine, the following reaction takes place:—

$$H_2S + 2I = S + 2HI,$$

or, expressed as ions:— $S'' + 2I = S + 2I'.$

That is, from sulphuretted hydrogen and iodine, hydrogen iodide and sulphur are formed. In this way an aqueous solution of hydrogen iodide can be easily prepared.

On the other hand, gaseous hydrogen iodide, on gently heating, acts on sulphur with formation of iodine and sulphuretted hydrogen gas. The cause of this difference lies in the fact that in the former case the hydrogen iodide dissolves in water and passes into its ions. The ions of hydriodic acid are much more stable than hydrogen iodide itself, and are therefore formed under the above conditions. In the second case, no water is present, and the greater stability of the sulphuretted hydrogen compared with the undissociated hydrogen iodide causes in that case the reversal of the process.

Decomposition of Sulphuretted Hydrogen by Heat.—Sulphuretted hydrogen itself is also not very stable. On being heated in a red-hot tube, it partially decomposes into sulphur and hydrogen. On the other hand, sulphuretted hydrogen is formed under the same conditions from its elements, so that we are here dealing with a chemical equilibrium according to the equation

$$H_2 + S \rightleftarrows H_2S.$$

Combustion of Sulphuretted Hydrogen.—Sulphuretted hydrogen readily burns in the air with a blue sulphur flame. If the gas contained in a cylinder be ignited, the walls of the cylinder become covered with a white coating of sulphur. This is due to the fact that the hydrogen of the sulphuretted hydrogen unites much more rapidly with the oxygen than the sulphur does. Therefore, if there is a scarcity of air, as in the interior of the cylinder, only the hydrogen burns and the sulphur separates out. In this case also, the sulphur is coloured white by reason of its state of fine division.

Analysis of Sulphuretted Hydrogen.—That sulphuretted hydrogen contains sulphur, is made evident by the experiment just described; the presence of hydrogen can be proved by converting this into water.

For this purpose a metallic oxide, *e.g.* mercury oxide, is heated in a current of dry sulphuretted hydrogen. The following reaction then takes place:—

$$HgO + H_2S = HgS + H_2O.$$

That is to say, mercury sulphide and water are formed. The latter can be easily collected in a cold receiver and identified by its properties.

Further, the hydrogen of sulphuretted hydrogen can be set free by metals. For example, if finely divided copper is heated in a current of sulphuretted hydrogen, the following reaction takes place:—

$$H_2S + Cu = CuS + H_2.$$

That is, copper sulphide and hydrogen are produced.

This property of decomposing sulphuretted hydrogen with formation of metallic sulphide belongs also to the noble metals, especially to mercury and to silver. For this reason, silver objects become black in contact with air containing sulphuretted hydrogen. To the same process is due the blackening of silver spoons which come into contact with boiled eggs or with egg-dishes.

Polysulphides.—When a solution of sodium sulphide is brought together with sulphur, the latter dissolves and the liquid becomes dark yellow in colour. By evaporation of the solution, compounds of the formulæ Na_2S_2 to Na_2S_5 can be obtained in the crystalline state. The solutions themselves behave quite similarly to those of sodium sulphide: they conduct electricity, and are, therefore, to be regarded as salt solutions. The ions are, on the one hand, sodion $Na^{\cdot}$, and, on the other hand, S_2'' to S_5'', or HS_2' to HS_5'.

The relations are similar to those in the case of iodine, where the ion I' can pass into the brown ion I_3' by taking up two further combining weights of iodine (p. 235).

Whether all the ions S_2'', S_3'', S_4'', S_5'', or, HS_2', HS_3', HS_4', HS_5' respectively, exist, or only one or a few of them, has not yet been established.

Hydrogen Persulphide.—The above solutions behave differently when acted on by acids, according as the acid is added gradually to the solution, or the solution poured into excess of acid. In the first case, sulphuretted hydrogen is evolved and the excess of sulphur separates out as milk of sulphur; this is the usual way of preparing milk of sulphur, sodium sulphide, however, being replaced by calcium sulphide. The reaction takes place according to the equation

$$Na_2S_5 + 2HCl = 2NaCl + H_2S + 4S,$$

when the pentasulphide is used, and in a corresponding manner with the other sulphides.

If, however, the concentrated solution of the sulphide be added to excess of hydrochloric acid, no sulphuretted hydrogen escapes, but oily drops separate out and unite to a yellow liquid. This has the composition H_2S_n, where n lies between 2 and 5. It is called hydrogen persulphide, and may be regarded as a mixture of the acids H_2S_2 to H_2S_5, corresponding to the salts Na_2S_2 to Na_2S_5.

The liquid is very unstable, readily undergoing spontaneous decomposition into sulphur and sulphuretted hydrogen. It exhibits, in this respect, some resemblance to hydrogen peroxide, for its decomposition is promoted by such substances as mechanically facilitate an evolution of gas. Differences are found only in so far as the hydrogen persulphide is but sparingly soluble in water.

* **Thermochemical Data.**—Sulphuretted hydrogen is formed from solid rhombic sulphur with development of 11 *kj*; on solution in water further 19 *kj* are developed, so that the heat of formation of dissolved sulphuretted hydrogen is 30 *kj*.

In the formation of hydrogen persulphide, an absorption of heat equal to 22 *kj* accompanies the taking up of the first atom of sulphur. In this respect, therefore, there is a similarity to hydrogen peroxide. The rest of the sulphur is dissolved without appreciable heat effect.

The heat of neutralisation amounts, for the first equivalent, to 32 *kj*, for the second, to zero. From this it likewise follows that the reaction consists essentially in the formation of the salt NaHS, or of the ions $Na^{\cdot} + HS'$, and that sodium sulphide in dilute solution reacts with the water according to the equation $Na_2S + H_2O = 2Na^{\cdot} + HS' + OH'$.

Further, it follows from the above value that the formation of the ions $H^{\cdot} + HS'$ from dissolved sulphuretted hydrogen, gives $32 - 57 = -25$ *kj*; that is, it takes place with strong absorption of heat, which is the opposite of what takes place in the case of hydrofluoric acid. For the equations

$$(Na^{\cdot} + OH')\text{ aq.} + H_2S\text{ aq.} = (Na^{\cdot} + HS')\text{ aq.} + 32\ kj$$
$$OH' + H^{\cdot} = H_2O + 57\ kj$$

yield, on subtraction of the lower from the upper and omission of the like terms,

$$H_2S\text{ aq.} = (H^{\cdot} + HS')\text{ aq.} - 25\ kj.$$

D. *Sulphur Dioxide and Sulphurous Acid*

Composition.—In the combustion of sulphur in air or oxygen, a gas is formed which has the well-known pungent smell of burning sulphur, and is a compound of sulphur with oxygen.

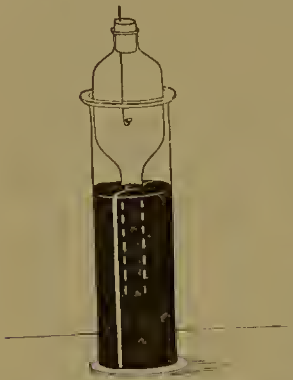

Fig. 87.

If the combustion is carried out in an enclosed space (*e.g.* in the apparatus, Fig. 87), it is found that the volume of the gas is not greatly different from that of the oxygen.[1] Since free oxygen is O_2, the compound which is produced in equal volume must also contain two combining weights of oxygen.

The molar weight of the gas has been found equal to 64 or somewhat over this, according to pressure and temperature. It contains, therefore, along with $2 \times 16 = 32$ parts of oxygen, 32 parts or one combining weight of sulphur, and its formula is SO_2.

Physical Properties.—Sulphur dioxide is a gas which, even at small pressures, exhibits deviations from Boyle's law, in the sense that as the pressure increases the volume diminishes more than proportionally to the pressure. Further, it can be liquefied by moderate pressure and cold. At atmospheric pressure, the temperature of a freezing mixture of ice and salt is sufficient; if sulphur dioxide be passed into a glass surrounded by this mixture, it condenses to a very mobile liquid as clear as water. In the following table is given the relation between pressure and temperature:—

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[1] As a rule, the volume is somewhat smaller, because along with the compound SO_2 there is also formed some SO_3, which combines with traces of moisture present, forming a non-volatile compound.

Temperature.	Pressure.	Temperature.	Pressure.
−30°	0·39 atm.	+5°	1·87 atm.
−25°	0·49 ,,	10°	2·26 ,,
−20°	0·63 ,,	15°	2·72 ,,
−15°	0·80 ,,	20°	3·24 ,,
−10°	1·00 ,,	25°	3·84 ,,
− 5°	1·25 ,,	30°	4·52 ,,
0°	1·53 ,,	40°	6·15 ,,

As can be seen, the boiling point at atmospheric pressure is − 10°. The critical magnitudes are: pressure 79 atm., temperature 157°.

Liquid sulphur dioxide is now placed on the market in metal cylinders, similarly to liquid chlorine. In cases where large quantities of the substance are required, the use of such cylinders is very convenient.

Behaviour towards Water.—Sulphur dioxide dissolves fairly abundantly in water. At higher temperatures the solubility follows to some extent the law of Henry. At room temperature one volume of water dissolves about 50 volumes of sulphur dioxide.

The aqueous solution smells strongly of the gas, which can be entirely expelled by boiling. Towards litmus, the solution shows the reaction of an acid; it therefore contains hydrion. Since sulphur dioxide does not contain any hydrogen, the acid must have been produced by the union of it with water, and therefore have the formula $SO_2 + nH_2O$. The value of n cannot be ascertained by an analysis of the liquid, since this contains excess of water. If, however, the liquid be neutralised with caustic soda and the sodium salt of the acid present prepared by evaporation, this is found to have the composition Na_2SO_3.

From this it is to be concluded that the acid has the composition H_2SO_3, and that $n = 1$.

Sulphurous Acid.—This acid, known not in the pure condition but only in solution, is called *sulphurous acid.* Sulphur dioxide is sometimes designated by this name, but that is incorrect. Rather, it must be called sulphurous acid anhydride, because it is formed from sulphurous acid by loss of water. As can be guessed from the formula, and as is found by analysis of the salts, sulphurous acid is a dibasic acid, and can form normal salts of the formula M_2SO_3 and acid salts $MHSO_3$, where M represents a combining weight of a monovalent metal.

Dissociation of Sulphurous Acid.—In the sense of the considerations set forth on p. 241, sulphurous acid is a comparatively weak acid, the second hydrogen of which shows very little tendency to pass into the ionic state. This is evident from the fact that the acid cannot be titrated with caustic soda and litmus. Even before the equivalent amount of base has been added, the colour changes slowly and continuously from red, through violet, to blue, without it being possible to distinguish a sharp transition. Accordingly, the aqueous solution of the normal sodium salt, which has been purified by repeated recrystallisation, also exhibits an alkaline reaction. This arises through the action of the water on the ions of the salt. According to the equation

$$2Na^{\cdot} + SO_3'' + H_2O = 2Na^{\cdot} + HSO_3' + OH',$$

the ion of the acid sulphites HSO_3' is formed at the expense of the water, hydroxidion being thereby also produced, which causes the characteristic blue coloration of litmus. This reaction, however, takes place to a less extent than in the case of sulphuretted hydrogen (p. 269).

Bleaching Action.—Sulphurous acid and its salts possess some properties which are of importance technically. Sulphurous acid bleaches various organic colouring substances, and is therefore used for the decoloration of silk and wool. These substances cannot be bleached with chlorine, because they thereby become hard and brittle.

To carry out the process of bleaching, the substances are hung up in a moist condition in chambers which can be closed, and in these the sulphur dioxide required is generated by the combustion of sulphur. When after some time the bleaching has taken place, the substances must be carefully washed in order to remove the transformation products of the colouring substances and the excess of sulphurous acid.

* This property can be clearly demonstrated by placing a number of coloured flowers near burning sulphur, and covering the whole with a glass bell-jar. In a short time all the flowers become white.

* The colour, however, is not completely destroyed, as in the case of chlorine, but can be restored. This takes place, to a certain extent, spontaneously, on standing some time in the air; more quickly by moistening the bleached blossoms with dilute sulphuric acid. Under these conditions blue colours which are turned red by acids do not, of course, appear again; in their place red appears.

Physiological Action.—Sulphurous acid has, further, a powerful action on vegetable organisms, from the highest orders down to the moulds and similar forms of life. This shows itself in an undesirable manner in the neighbourhood of foundries and chemical works in which sulphur dioxide is generated and in part diffused through the air, in the fact that vegetable growth more or less completely dies out. Even the sulphur contained in coal produces similar effects in towns. This important property of sulphurous acid finds useful application in the "curing" of wine and beer for the purpose of keeping away mould and other organisms, which would have a detrimental action on these liquids. This is the purpose of the process of sulphuring wine casks, *i.e.* of burning sulphur in the interior of them, which has been in vogue from remote times. For similar purposes large quantities of sulphurous acid salts are used in breweries.

Preparation.—The preparation of sulphur dioxide and of the sulphurous acid salts or the sulphites, is carried out by burning sulphur or metallic sulphides by means of the oxygen in the air. Sulphur dioxide is formed, and this is either employed as such or is converted into other compounds. Since an aqueous solution saturated under atmospheric pressure contains only 10 per cent of sulphurous acid, it is better to prepare a concentrated solution of acid sodium sulphite, $NaHSO_3$, by the action of sulphur dioxide on sodium carbonate. This is prepared commercially, and is employed for the purposes specified above. This solution is also the most convenient means for preparing sulphur dioxide for laboratory purposes. For this, it is only necessary to place concentrated sulphuric acid in a flask fitted with dropping funnel and delivery tube, and to allow bisulphite solution to drop in from the dropping funnel. The sodium salt of sulphuric acid is formed, and the sulphurous acid simultaneously formed decomposes into water, which remains behind, and sulphur dioxide, which escapes.

Reducing Actions.—Sulphurous acid readily absorbs oxygen, and passes into another compound which has the composition H_2SO_4, and is called sulphuric acid. Sulphurous acid is a reducing agent, because it can also withdraw the oxygen necessary for this transformation from oxygen compounds. The oxygen can also be removed from water if an opportunity is given to the hydrogen of entering into another combination. Sulphurous acid then acts not by withdrawing oxygen but by adding hydrogen. An example of this last process is afforded by the action of sulphurous acid on iodine, which takes place according to the equation

$$H_2SO_3 + 2I + H_2O = H_2SO_4 + 2HI.$$

The iodine passes, therefore, into hydriodic acid. Since very small quantities of free iodine can be detected by means of starch (p. 232), the above reaction can be used for the volumetric determination of iodine with sulphurous acid, or of sulphurous acid with iodine. This method, which was formerly much employed, has now been abandoned in favour of more convenient methods. The inconvenience of the method lies in the fact that the composition of the solutions of sulphurous acid is continually undergoing change, owing to escape of the gas and to oxidation by the oxygen of the air. Solutions of sulphurous acid salts, which act on iodine in the same way, do not have the first disadvantage but they have the second. The spontaneous oxidation by the oxygen of the air can, however, be almost entirely abolished by adding to the solution a small quantity of alcohol, glycerine, sugar, or similar substances. So small a quantity as $\frac{1}{10000}$ to $\frac{1}{1000}$ of the weight of the solution is sufficient for this purpose. The substance itself undergoes no change; the action has, therefore, to be designated as a catalytic one.

Pyrosulphurous Acid.—From the hot, concentrated solutions of the acid sulphites of the alkali metals, salts crystallise out which do not have the composition of acid salts, because they contain no hydrogen. The potassium salt, more especially, forms very readily, and is found to have the composition represented by the formula $K_2S_2O_5$. On comparing this formula with that of the acid sulphites, $KHSO_3$, it is seen that the salt has been formed from this, with the loss of the elements of water—

$$2KHSO_3 = K_2S_2O_5 + H_2O.$$

The corresponding acid must, accordingly, have the formula $H_2S_2O_5$. It can be looked upon as a compound of sulphurous acid and sulphur dioxide—

$$H_2SO_3 + SO_2 = H_2S_2O_5.$$

If, however, it be attempted to prepare this acid from the potassium salt, only the ordinary sulphurous acid is obtained. The new acid, therefore, passes at the moment of its liberation into sulphurous acid, or, what is perhaps more correct, the sulphurous acid also contains small amounts of the acid $H_2S_2O_5$ along with the ordinary acid; the different forms, however, pass so quickly into one another that they cannot be investigated individually.

The acid $H_2S_2O_5$ is called *pyrosulphurous acid*, and its salts are called pyrosulphites. The name is due to the fact that a similar derivative of phosphoric acid has been obtained by heating that acid.

* **Thermochemical Relations.**—The combustion of sulphur to gaseous dioxide develops 297 *kj*, the dissolution of the latter in water, further 32 *kj*, so that the heat of formation of the aqueous acid is 329 *kj*. When one equivalent of caustic soda is added to the solution, 67 *kj* are developed; a second equivalent yields further 55 *kj*. From this it follows that the formation of the ions $H^\cdot$ and HSO_3' from the undissociated acid, H_2SO_3, takes place with a development of heat of more than 13 *kj*; since the acid is already slightly dissociated, the whole amount of heat does not show itself. The second dissociation, $HSO_3' = H^\cdot + SO_3''$, appears to take place without any considerable heat effect, since the heat of neutralisation 55 *kj* is very near to the normal 57 *kj*.

E. *Sulphur Trioxide and Sulphuric Acid*

Sulphur Trioxide.—Although sulphur dioxide is not the highest compound of oxygen with sulphur, it is essentially the only one which is produced in the direct interaction, *i.e.* in combustion, even when oxygen is present in great abundance. A higher oxide of sulphur, sulphur trioxide, SO_3, is formed at the same time only in very small amount, mixing in the form of a white mist with the gaseous dioxide.

Nor is it possible to prepare any considerable amount of trioxide by heating, say, the dioxide with oxygen. This is not in any way due to the trioxide being an unstable compound which readily decomposes into the dioxide and oxygen: the reverse is the case. Rather, we must assume that the velocity with which dioxide and oxygen combine to trioxide, is exceedingly small even at comparatively high temperatures. The rapid combination of sulphur dioxide and oxygen can be effected by the same substance by which the union of oxygen and hydrogen is accelerated (p. 104). If a mixture of the two gases be passed through a heated tube containing finely divided platinum, union takes place. From the tube there escapes a vapour which in moist air forms dense white fumes with a choking smell, and which can be condensed to a colourless liquid possessing very striking properties.

Manufacture.—The combination of sulphur dioxide and oxygen to trioxide, with the help of platinum, has been recently carried out on a manufacturing scale and begins to be of exceeding importance. At first it was employed only for the preparation of the trioxide itself, which is applied fairly largely in the preparation of organic dyes.

For this purpose, a mixture of steam, sulphur dioxide, and oxygen was generated by the decomposition of sulphuric acid at a high temperature, $2H_2SO_4 = 2H_2O + 2SO_2 + O_2$. This was freed from the water vapour by drying with sulphuric acid and then passed over heated, finely divided platinum, when combination to trioxide took place, $2SO_2 + O_2 = 2SO_3$. The reason that the sulphur dioxide was not prepared simply by combustion was that the impurities in the gas soon rendered the platinum inefficient.

Quite recently, however, the method has been discovered of carrying out the purification of the crude sulphur dioxide so successfully that that disadvantage is avoided. Sulphur trioxide in any desired amount can be directly obtained by the action of metallic platinum, from a mixture of sulphur dioxide and air such as is obtained by the combustion of ores containing sulphur. This preparation can be carried out so cheaply that it is used for the preparation of sulphuric acid, and will in all likelihood replace the method hitherto employed, which will presently be described.

Properties.—Sulphur trioxide is a colourless, mobile liquid, which boils at 46° and has, therefore, even at the ordinary temperature, a considerable vapour pressure. When cooled it solidifies to a transparent, ice-like mass which melts at 15°.

Besides this, there is another form known which is always formed when the trioxide is kept for a long time. It has the appearance of an opaque, white, asbestos-like mass, which on being heated does not melt but passes directly into the vaporous state.

So far as can be judged from the imperfect observations, we are here dealing with two forms of different stability, such as occurred in the case of iodine chloride (p. 238). One of these forms, the opaque, is stable, the other is unstable, and in separating from the liquid state, the latter is first formed in accordance with the rule given on p. 207.

The relations observed in the case of the two forms of sulphur differ from those met with here by the fact that there is in this case no transition point, at which the stability of the two forms changes, but throughout the whole known range, the one form is stable, the other unstable. It is, therefore, to be expected that the more stable, opaque form of sulphur trioxide will have the smaller vapour pressure, and will be formed from the other with development of heat. Experiments on this point, however, are as yet wanting.

Action of Water.—In the air, sulphur trioxide forms dense, white fumes. This is due to the fact that the vapours of the readily volatile substance combine with water to form the very slightly volatile sulphuric acid: $SO_3 + H_2O = H_2SO_4$.

The sulphuric acid, accordingly, passes at once into the liquid form, and the very small drops of liquid which are formed constitute the fumes.

The great tendency to unite with water becomes evident on bringing the substances together directly. On allowing some trioxide to fall into water, a hissing noise is produced, as when red-hot iron is immersed. At the point of contact between trioxide and water, so much heat is developed that a portion of the water is vaporised. This vapour is again condensed to liquid by the rest of the water, and these violent movements are the cause of the hissing sound.

Sulphur trioxide also acts on various other substances, with the formation of compounds, and it, therefore, finds manifold application in chemical technology. For these purposes it is usually employed not in the pure state but dissolved in sulphuric acid. The solutions containing 40 per cent and over are solid at the ordinary temperature, and become liquid only on being gently warmed.

The substance which crystallises from the solutions, has the composition $H_2S_2O_7$ equal to $H_2SO_4 + SO_3$. It is, therefore, a compound of sulphuric acid with sulphur trioxide.

Sulphuric Acid.—Sulphurous acid, or sulphur dioxide plus water, is slowly converted by the oxygen of the air into sulphuric acid: $2H_2SO_3 + O_2 = 2H_2SO_4$. The process, however, although accompanied by a considerable diminution of the total as well as of the free energy, takes place, strange to say, only very slowly—so slowly, indeed, that it cannot be made use of for manufacturing purposes. For this reason, the sulphuric acid was formerly prepared in another way, viz., by strongly heating iron vitriol or sulphate of iron. The process is, chemically, not very simple, and the details of it will be given under iron. It has, at the present day, only an historical importance, since it is no longer used.

The method still chiefly employed at the present time (cf. p. 283) depends on the oxidation of sulphur dioxide or sulphurous acid, but this is accelerated by a particular expedient to such an extent that it has become a productive manufacturing method.

The method was developed from experiments made to replace the oxygen of the air by more quickly acting oxidising agents. Sulphur was burned with the addition of potassium nitrate or saltpetre. This substance has the formula KNO_3; it contains, therefore, a large amount of oxygen, with which it readily parts. In these experiments it was found that much more sulphuric acid was produced than could have been formed from the oxygen of the saltpetre. The cause of this was found to be that the oxidation of the sulphurous acid by the oxygen of the air takes place much more quickly in the presence of the gaseous oxygen compounds of nitrogen which are produced under the above conditions than when it is alone.

Manufacturing Process.—The above-mentioned process then amounted to this: Sulphur dioxide was formed by the combustion of sulphur, and the gas was mixed with air and water vapour in the amount necessary for the formation of sulphuric acid, the production of which was sufficiently accelerated by the addition of oxides of nitrogen. The various stages through which the process has passed cannot be described here; it will be sufficient to give a description of the arrangement of a present-day sulphuric acid manufactory. The sulphur dioxide is, at present, generated only to a small extent from sulphur itself; for its formation the sulphur compounds of iron are chiefly used. These are burned in suitable furnaces, forming iron oxide, which remains behind, and sulphur dioxide, which escapes. Large quantities of sulphuric acid are also formed from other ores containing sulphur, which, for the purpose of obtaining the metals in them, are "roasted," *i.e.* heated with access of air. The sulphur passes into sulphur dioxide, and the metals form oxides.

The hot mixture of sulphur dioxide and air is first of all led into an empty chamber, where the small, solid particles carried over with the gas, "flue-dust," are deposited.

The gases then enter at the foot of a tower filled with acid-resisting stones and are met by a counter-stream of crude, dilute sulphuric acid, such as is formed in this process. By this arrangement the hot gases are cooled by causing the evaporation of the water contained in the dilute sulphuric acid; the acid is thereby concentrated.. At the same time, the acid is freed from the oxides of nitrogen which it contains (*vide infra*), and these are again brought into the process. In this way, not only is a loss of these comparatively valuable substances avoided, but the sulphuric acid is at the same time freed from an impurity which would be very detrimental in its further treatment and application.

From the tower, the gases pass into several large chambers lined entirely with lead plates. (Lead is attacked by sulphuric acid to a comparatively slight extent.) Into these chambers, steam and oxides of nitrogen are also introduced; oxidation to sulphuric acid occurs, and this falls as a fine rain to the bottom of the chamber.

From the last chamber there escapes not only the nitrogen of the used-up air, but also the oxides of nitrogen present, so far as they have not been absorbed by the dilute acid formed in the chambers, the "chamber acid." In order that these oxides may not be lost, they are led through a second tower in which concentrated sulphuric acid is trickling in an opposite direction. The latter readily dissolves large quantities of the oxides of nitrogen, and so retains this valuable material. The atmospheric nitrogen passes into a large chimney, which maintains the draught through the whole series of apparatus. The concentrated sulphuric acid charged with the oxides of nitrogen is introduced into the first tower, where the oxides of nitrogen are given off.

Action of the Oxides of Nitrogen.—As to the cause of the acceleration of the sulphuric acid formation by the oxides of nitrogen, a theory has been in existence for a hundred years. According to this, the cause lies in the alternate reduction of the oxides by the sulphur dioxide and their re-oxidation by the oxygen of the air. The details of this theory cannot be discussed till the oxides of nitrogen are treated. Since the oxides of nitrogen are found at the beginning and the end of the process in the same condition, and are not used up, we must at this point be satisfied with designating the accelerating action as a catalytic one.

Concentration of the Acid.—The acid obtained by this method contains about 65 per cent of acid and 35 per cent of water. This amount of water, in the form of steam, must be introduced into the lead chamber in order that the formation of sulphuric acid shall take place quickly and regularly. For most of the applications of sulphuric acid, however, this water must be removed.

This is effected in the first place in flat lead pans which are heated from above. When the sulphuric acid attains a concentration of 80 per cent, it begins to attack the lead. It is then evaporated further in flat platinum retorts. At first, almost pure water passes over, but when the acid has reached a concentration of 98·5 per cent, the vapour has nearly the same composition as the liquid, and further concentration becomes impossible. Before the acid has reached this strength, it is run into carboys, in which it is transported.

Crude and Pure Acid.—The crude sulphuric acid is not pure. The chief impurity which it contains is sulphate of lead. This is more readily soluble in concentrated than in dilute sulphuric acid, and separates out, therefore, as a white precipitate on mixing the acid with water. Further, the acid is often coloured brown from the presence of dissolved organic compounds from particles of straw or wood which have fallen into it. As a rule, also, oxides of nitrogen, derived from the preparation, and compounds of arsenic, from the metallic sulphides employed, are present.

Pure acid is obtained by the distillation of the impure. The boiling point of sulphuric acid is fairly high, viz., 338°.

The acid obtained by distillation does not have exactly the composition H_2SO_4, but contains a few per cent of water. This is connected with the fact that the vapour of sulphuric acid is not a single substance, but a mixture of sulphur trioxide, the anhydride of sulphuric acid, and water vapour. This is seen, in the first place, from the vapour density, which is not 98, corresponding to the formula H_2SO_4, but only the half, corresponding to the density of a mixture $H_2O + SO_3$. Further, the presence of the components of the mixture can be shown by subjecting the vapour of sulphuric acid to *diffusion*. If, for example, the vapour alone be kept some hours in an open flask at a temperature above 350°, the lighter water vapour diffuses away more quickly, and, on cooling, there is found in the flask a mixture of sulphuric acid and sulphur trioxide.

If one recall the great violence with which the combination of sulphur trioxide with liquid water takes place, one must inquire as to the reason why these substances do not combine at all in the vaporous state. The reason is to be found in the fact that sulphuric acid can form ions only in aqueous solution. In the vapour, no ions are present, for it is a non-conductor of electricity. Sulphuric acid, now, is a strong acid, *i.e.* it has a great tendency to form ions; for this reason sulphur trioxide acts strongly on liquid water, in which it can form sulphanion, but has no action on water vapour, with which that is not possible.

Solid Sulphuric Acid.—At lower temperatures, sulphuric acid forms crystals which melt at 10·5°. If the acid contain water, the melting point is lower in proportion to the amount of water. Super-cooling, also, occurs to a large extent, so that the ordinary, somewhat hydrated acid must be strongly cooled in order to obtain the crystals.

Crystallisation affords us a good means of obtaining the pure acid H_2SO_4 from the hydrated acid. This is cooled down until the greater part has crystallised, and the liquid portion is discarded. The crystals are melted and the acid again made to partially solidify, and this method of purification is repeated till the melting point 10·5° is reached and no longer rises.

Sulphuric acid, in the liquid state, is a rather thick liquid having a high specific gravity, viz. 1·838 at 15°. It fumes somewhat in the air, for since the constant boiling mixture contains rather more water, the vapour of pure sulphuric acid must contain excess of anhydride.

Aqueous Sulphuric Acid.—On dissolving sulphuric acid in water, a large amount of heat is developed, so that, under certain circumstances, the liquid may boil. The cause of this is that the passage of sulphuric acid into its ions is accompanied by a very considerable evolution of heat. For the pure acid, H_2SO_4, scarcely conducts the current, and only on being diluted with water does it become a very good conductor. On dissolving sulphur trioxide in a large quantity of water, 164 *kj* are developed. On dissolving sulphuric acid, H_2SO_4, in much water, the heat development is 75 *kj*. From this it follows that the combination of the trioxide with one mole of water, or the reaction $SO_3 + H_2O = H_2SO_4$, yields 89 *kj*.

Further, on solution, the total volume diminishes very considerably. In a tube one metre long and about 1 cm. wide, closed at one end, a column of concentrated sulphuric acid is covered with an equally high column of pure water, the tube closed with a rubber stopper, and the two liquids mixed by inverting the tube. So much heat is developed in the reaction that the hand must be protected with a cloth. On cooling, the level of the liquid is about 3 cm. lower than before.

On account of this contraction, no simple relation exists between the strength of a dilute sulphuric acid solution and the extensity, or the density, and recourse must therefore be had to a table when it is desired to determinate the strength from the density. The following is such a table :—

DENSITY AND COMPOSITION OF SOLUTIONS OF SULPHURIC ACID

d.	H_2SO_4 per cent.	*d.*	H_2SO_4 per cent.
1·000	0·09	1·500	59·70
1·050	7·37	1·550	64·26
1·100	14·35	1·600	68·51
1·150	20·91	1·650	72·82
1·200	27·32	1·700	77·17
1·250	33·43	1·750	81·56
1·300	39·19	1·800	86·90
1·350	44·82	1·810	88·30
1·400	50·11	1·820	90·05
1·450	55·03	1·830	92·10

In the same way all the other properties of sulphuric acid change continuously with the composition. The fact, more especially, that the vapour pressure of solutions of sulphuric acid containing only a small amount of water is very small, has a practical application. Sulphuric acid is used for drying gases, and indirectly also for drying other objects (cf. p. 124).

Acids containing somewhat more water have been much used for the purpose of giving a definite, very small pressure of aqueous vapour.

The Ions of Sulphuric Acid.—Being a dibasic acid, sulphuric acid can form two kinds of anions, viz., the monovalent HSO_4' and the divalent SO_4''. Concentrated solutions of the acid chiefly contain the former; the greater the dilution, the more does this dissociate into the dibasic ion and hydrion.

Applications of Sulphuric Acid.—In the laboratory, and still more in the arts, sulphuric acid is a substance of immense importance and manifold application. Its importance for the chemical industry has been justly compared with that of iron for the engineering industry. The manifold application of sulphuric acid depends on the fact that it can be used in two ways for obtaining other acids from their salts. Since it is, as a rule, only the *salts* of the various acids that are got directly, and from these the free acids must then be obtained, an acid suitable for this object finds a very varied application.

The use of sulphuric acid for this purpose depends on the combination of several circumstances. Apart from its cheapness, the fact that it is a strong acid, *i.e.* one largely dissociated into ions, and has a high boiling point, is the determining factor.

Certainly, on making a comparison, it is found that in equivalent solutions, *i.e.* solutions containing equal amounts of hydrogen, hydrochloric acid is a better conductor than sulphuric acid, and that the former, therefore, is more dissociated. However, the somewhat smaller degree of dissociation of sulphuric acid (cf. p. 242) is more than compensated for by its small volatility. Thus, hydrochloric acid is prepared from sodium chloride by means of sulphuric acid, according to the equation

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

The possibility of expelling (or more exactly, of generating) the stronger acid from its salts by means of the weaker, depends on the difference of the volatility of the two acids. When sulphuric acid acts on sodium chloride, only a small quantity of hydrochloric acid is at first formed, and the reaction would stop, *i.e.* a chemical equilibrium would be established, if all the substances remained together. Even on gentle heating, however, the hydrochloric acid passes off in the gaseous state. The equilibrium is thereby disturbed, fresh hydrochloric acid must be formed, and, therefore, fresh sodium chloride be decomposed. If this hydrochloric acid be also removed, the process goes on until, finally, all the sodium chloride is decomposed or all the sulphuric acid is used up (cf. p. 205).

In the decomposition of sodium chloride by sulphuric acid, and in similar processes, two stages can be clearly distinguished. The first half of the decomposition always takes place much more easily, *i.e.* at a lower temperature, than the second. This depends on the dibasic nature of sulphuric acid. The process is separable into two stages, represented by the following equations :—

$$H_2SO_4 + NaCl = NaHSO_4 + HCl$$

and

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl.$$

As in the case of all polybasic acids, the one combining weight of hydrogen splits off first and most readily; the splitting off of the second occurs with much greater difficulty. For this reason, even when two combining weights of sodium chloride are present, there is, at first, only the acid sodium sulphate formed, according to the first equation, and one combining weight of sodium chloride remains. Not until this reaction is essentially over, and a higher temperature is employed, does the second process, the decomposition of the sodium chloride by the acid sodium sulphate, take place, with formation of the normal sulphate.

Continuation.—Sulphuric acid can be used also in a second way for the preparation of free acids from their salts. With some metals, especially barium (Ba) and lead (Pb), it can form very difficultly soluble salts. Therefore, if aqueous solutions of the barium or lead salt of the acid in question be mixed with sulphuric acid, barium or lead sulphate is formed, and separates out in the solid state, while the acid remains in solution. In this way, for example, chloric acid, $HClO_3$, is obtained (p. 213).

Analytical Test.—This same circumstance, the difficult solubility of barium sulphate, is employed for the detection and estimation of sulphuric acid and its salts; in general, of the ion SO_4''. Whenever barion, $Ba^{\cdot\cdot}$, comes together with the ion SO_4'', the precipitate of barium sulphate ($BaSO_4$) separates out. Since sulphuric acid is a fairly strong acid, the small solubility of barium sulphate is not increased to any considerable extent by the presence of free acids (p. 273). The reaction, therefore, is also given in acid solutions. Nor is there any other substance by means of which barium sulphate is rendered soluble in aqueous liquids. This reaction, therefore, is a very certain criterion for the presence of SO_4''-ion, and an error can arise only from the fact that selenic acid (*vide infra*), which is very similar to sulphuric acid, yields a similar, difficultly soluble precipitate with barium salts. When we come to selenic acid, however, we shall show how such an error can be excluded.

The question may be asked, if the two different ions, HSO_4' and SO_4'', do not, in conformity with the difference of their composition, have different properties and characteristics. As to the former, there is no doubt but the detection of these differences is not easy, since it presupposes a knowledge of the proportions of both ions in a given solution. Although this problem is not insoluble, still it is so complicated that it cannot be discussed here.

On the other hand, for the detection and the estimation of sulphuric acid by barium compounds, it is a matter of indifference in what proportions the ions HSO_4' and SO_4'' are present in a solution. By precipitation as barium sulphate, certainly, only SO_4''-ion is at first removed; so soon, however, as this takes place, a fresh amount is formed from HSO_4'-ion, which is also precipitated, and so on until practically all the sulphuric acid has been precipitated. Only when the concentration of the hydrion is very great, that is, when the solution is very acid, does a measurable quantity of HSO_4'-ion remain undissociated, and is not precipitated. Hence the rule that the precipitation of barium sulphate must not be carried out in a too acid solution.

Decompositions of Sulphuric Acid.—Sulphuric acid is a fairly stable substance. It undergoes oxidation to a higher stage only under quite special conditions by means of the electric current. Reduction takes place more readily, and use is sometimes made of such processes for the preparation of sulphur dioxide. Such reduction occurs, for example, on heating sulphuric acid with copper.

Copper is a divalent metal, the sulphate of which has the formula $CuSO_4$. On heating copper with sulphuric acid, the usual displacement of hydrogen by metal first takes place—

$$Cu + H_2SO_4 = CuSO_4 + H_2.$$

The hydrogen, however, is not evolved, but is oxidised at the expense of the oxygen of a second mole of sulphuric acid; this is reduced to sulphurous acid, which immediately decomposes into sulphur dioxide and water. In formulæ,

$$H_2SO_4 + H_2 = 2H_2O + SO_2.$$

The two equations can be combined into one, and we obtain

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

Mercury and silver behave similarly to copper. In the case of zinc, the reduction goes still further, sulphuretted hydrogen being formed under certain circumstances—

$$5H_2SO_4 + 4Zn = 4ZnSO_4 + 4H_2O + H_2S.$$

This reduction occurs only when the solutions are fairly concentrated. Dilute sulphuric acid reacts with zinc, with formation of hydrogen—

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Pyrosulphuric Acid.—The compound of sulphuric acid with trioxide, $H_2S_2O_7$, mentioned on p. 284, is a special acid, to which the name of pyrosulphuric acid has been given. For the compound not only exists itself, but the corresponding salts can be prepared, *e.g.* the sodium salt $Na_2S_2O_7$. The salts are obtained by heating the acid sulphates, *e.g.*

$$2HNaSO_4 = Na_2S_2O_7 + H_2O.$$

If heated more strongly, the salts lose sulphur trioxide and pass into normal sulphates, *e.g.*

$$Na_2S_2O_7 = Na_2SO_4 + SO_3.$$

It must, however, be specially noted that in aqueous solution the corresponding ion, S_2O_7'', is not known. On solution, the pyrosulphates take up water and pass into the acid sulphates

$$Na_2S_2O_7 + H_2O = 2NaHSO_4,$$

and the process apparently proceeds so quickly that it has not hitherto been possible to distinguish between the solution of a pyrosulphate and an equally strong solution of the corresponding acid sulphate. From experience gained from other acids of a similar composition, however, cases are known in which differences can be readily detected between the ions of the normal and of the pyro-acids.

* **Thermochemical Relations.**—The heat of formation of liquid sulphur trioxide from its elements is 432 *kj*. Its heat of vaporisation is 49 *kj*; its heat of formation in the vapour form amounts, therefore, to 383 *kj*. Since the heat of formation of the dioxide amounts to 297 *kj*, this would, by combustion to the trioxide, develop 86 *kj*. In spite of this great heat evolution, this process takes place only very slowly and incompletely, and, in order to be of use for manufacturing purposes, it must be accelerated by catalysers, *e.g.* platinum.

The trioxide dissolves in water with great development of heat, amounting to 164 *kj*. Sulphuric acid, H_2SO_4, dissolves in water with development of 75 to 88 *kj*; at great dilution the heat effect still increases to a measurable extent. By the formation of sulphuric acid, therefore, from trioxide and water, about 85 *kj* are developed.

The heat of neutralisation of sulphuric acid varies according as the acid or the normal salt is formed. If a mole of caustic soda is added to a mole of sulphuric acid in dilute solution, so that the acid salt is formed ($H_2SO_4 + NaOH = NaHSO_4 + H_2O$), 62 *kj* are developed; the second mole of caustic soda yields the considerably greater evolution of heat, viz., 69 *kj*.

From the large amount of heat which is developed on dissolving sulphuric acid in water, one may conclude that the dissociation of the acid into its ions is accompanied by a great development of heat. In the semi-normal solutions used in the experiments, the first stage of the dissociation $H_2SO_4 = H^{\cdot} + HSO_4'$ is fairly complete, and the second stage, $HSO_4' = H^{\cdot} + SO_4''$, has proceeded about half way. By the action of the first mole of caustic soda, the normal heat of neutralisation, 57 *kj*, is first of all developed; the excess of 5 *kj* is due to the dissociation of a further portion of the HSO_4'-ion into $H^{\cdot} + SO_4''$, owing to the consumption of hydrion. On neutralisation with the second mole of caustic soda, the dissociation becomes complete, since the neutral solution contains only SO_4''-ion, and the excess of 12 *kj* above the normal value is due to this dissociation.

The appropriate experiments for the exact calculation of the heats of dissociation are as yet wanting, and it can only be asserted that in both stages the dissociation in the case of sulphuric acid takes place with considerable development of heat, viz., 20 to 40 *kj*.

F. *Other Oxygen Acids of Sulphur*

Persulphuric Acid.—On electrolysing a dilute solution of sulphuric acid, hydrogen and oxygen are evolved in the same proportions in which they form water, hydrogen being evolved at the cathode and oxygen at the anode. For this reason the process was for a long time looked upon as if water were the electrolyte, and the purpose of the sulphuric acid only to make the water "a better conductor." Apart from the fact that no reason is known why the sulphuric acid should make the water a better conductor, it is now known that in solution the ions $2H^{\cdot}$ and SO_4'' of sulphuric acid are present to a preponderating extent and effect the conduction.

According to this, the formation of hydrogen at the cathode is easily understood. The formation of oxygen is most simply (although perhaps not quite correctly) explained by assuming that the ion SO_4'' is discharged at the anode. Since a chemical compound SO_4 (as non-ion) does not exist, interaction takes place with the water present with regeneration of sulphuric acid and evolution of oxygen—

$$2SO_4 + 2H_2O = 2H_2SO_4 + O_2.$$

Support is given to this view by the behaviour of more concentrated sulphuric acid on electrolysis. If such an acid with a concentration of about 50 per cent is subjected to the action of the electric current, being kept cool the while, hydrogen appears as before at the cathode. At the anode, however, no oxygen makes its appearance, but the sulphuric acid becomes mixed with a new compound which has different properties, and, in the pure state, proves to be an acid of the formula $H_2S_2O_8$.

The formation of this substance, *persulphuric acid*, is explained as follows. In the concentrated solution, the sulphuric acid is essentially dissociated in accordance with the first stage into $H^{\cdot}$ and HSO_4'. The ion HSO_4' is discharged at the anode and passes into persulphuric acid $H_2S_2O_8$, its molar weight being doubled. The formation of this acid takes place still more readily by the electrolysis of one of the acid salts instead of sulphuric acid. These likewise yield the ion HSO_4', *e.g.* $NaHSO_4 = Na^{\cdot} + HSO_4'$. The potassium salt of persulphuric acid, more especially, is rather difficultly soluble, and on electrolysis of the acid sulphate soon separates out as a crystalline mass.

This experiment is best performed in the apparatus shown in Fig. 88.

Persulphuric acid and its salts readily lose oxygen and pass into sulphuric acid and sulphates respectively. They therefore act as oxidising agents, and as such they have a manifold technical application. Their oxidising action can be shown by adding them to a solution of potassium iodide. Free iodine separates out according to the equation

$$K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2,$$

which can be recognised by the solution becoming of a brown colour.

Hydrosulphurous Acid.—Besides the acids already described, sulphur forms with oxygen and hydrogen a large number of other compounds, all of which have acid properties. Some of these are of considerable technical and scientific importance; others have, as yet, found no notable application.

As the lowest stage, there may, in the first place, be mentioned hydrosulphurous or hyposulphurous acid.[1] The zinc salt of this is formed by the action of metallic zinc on sulphurous acid, in accordance with the equation

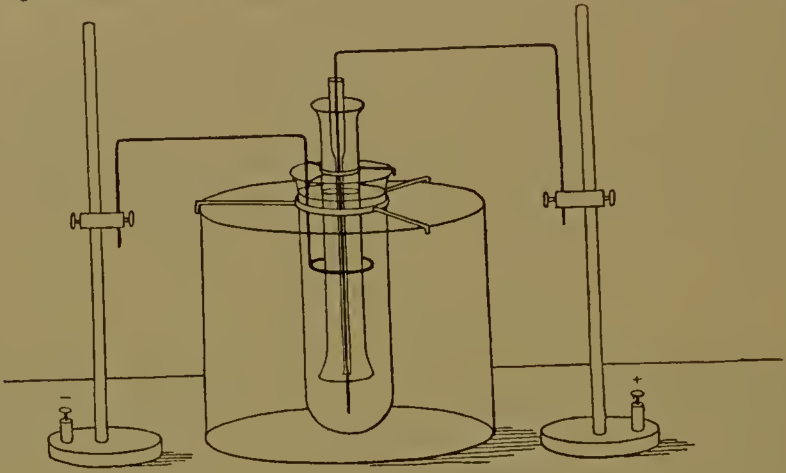

FIG. 88.

$$2SO_2 + Zn = ZnS_2O_4.$$

According to this, the free acid (not known in the pure state) would have the formula $H_2S_2O_4$.

The most striking property of the acid is its quick reducing action. Its total action cannot, of course, be greater than that of zinc, which was used to reduce the sulphurous acid; it is, however, distinguished from zinc by the velocity of its action on many substances. Thus, for example, gaseous oxygen is almost instantaneously absorbed by the solution, and it is therefore used for the volumetric determination of the free oxygen dissolved in water or other liquid. As indicator in such determinations, the organic colouring matter indigo is used; this is reduced by hydrosulphurous acid to a colourless compound, but its original blue colour is restored by oxygen.

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[1] Since the name hyposulphurous acid is also used for the acid to be presently discussed, thiosulphuric acid, it is more expedient to retain the designation hydrosulphurous acid, although it is not formed in accordance with the systematic nomenclature.

Thiosulphuric Acid.—Just as the ion SO_3'' of sulphurous acid readily takes up oxygen and passes into the ion of sulphuric acid, SO_4'', so also in contact with sulphur it takes up one combining weight of that element and is transformed into the ion S_2O_3'', which is known as that of *thiosulphuric acid.* It can be regarded as having a constitution similar to that of sulphuric acid by supposing that the atom of sulphur taken up "enters at the same point" or assumes the same function as the last atom of oxygen in the sulphuric acid. Even although such a view contains much that is indefinite, still it gives expression to some of the facts found by experiment.

One very striking fact is the instability of free thiosulphuric acid, or, in other words, the incompatibility of the ions S_2O_3'' and $H^{\cdot}$. As has been already mentioned, the sodium salt is very readily formed by the action of sulphur on sodium sulphite; it is only necessary to warm a concentrated solution of this salt with sulphur to immediately bring about the reaction

$$Na_2SO_3 + S = Na_2S_2O_3,$$

or, writing the ions,

$$SO_3'' + S = S_2O_3''.$$

If, however, the solution is acidified, turbidity occurs after a few moments, owing to the separation of sulphur and formation of sulphurous acid—

$$S_2O_3'' + H^{\cdot} = HSO_3' + S.$$

The reaction is fairly sensitive to hydrion; it is brought about even by the quite small amounts yielded by weak acids. For this reason, perfectly clear solutions of sodium thiosulphate soon become turbid not only on the addition of a few drops of some acid, but even by the action of the weak carbonic acid (*vide infra*) contained in the air, which acts in the same way. Such solutions, therefore, cannot be kept clear if the air is allowed access, and although the action is a slow one, still the easily recognisable bluish-white turbidity, due to traces of sulphur which have separated out, makes its appearance after some time—hours or days.

* The decomposition is retarded or wholly prevented by the presence of sulphites. The greater the amount of sulphite present, the more hydrion may be added, *i.e.* the more strongly may the solution be rendered acid, without sulphur separating out.

* The explanation of this behaviour is found if we consider the equation of the reaction taking place between the ions present, which runs

$$S_2O_3'' + H^{\cdot} = HSO_3' + S.$$

There is thus formed the primary ion of sulphurous acid along with sulphur; and, since this ion is fairly stable, the reaction takes place essentially in the sense of the equation, from left to right, until the concentration of the hydrion has become very small.

* If, however, the concentration of the hydrosulphosion is increased, a larger quantity of hydrion is required in order that the equilibrium may exist, *i.e.* the solution can contain a definite amount of acid without sulphur separating out. On this depends the protective action which is exercised by the addition of sulphurous acid or sodium sulphite to thiosulphate; the solution can be all the more strongly acidified, the greater the amount of sulphite it contains.

* A further remarkable property of the process is that it requires an appreciable time. If dilute solutions (say 0·1 – normal) of sodium thiosulphate and hydrochloric acid be mixed, the liquid remains, at first, quite clear, and only after half a minute does a turbidity, due to separated sulphur, suddenly appear. The more dilute the solutions, the longer is the time required; also, the time increases as the temperature sinks.

* This phenomenon must by no means be interpreted as if the thiosulphuric acid remained a certain time unchanged in the solution and then underwent a sudden decomposition. On the contrary, we must assume that the decomposition begins immediately the liquids are mixed. The sulphur formed, however, remains at first in solution, and only after it has reached a definite concentration, or has experienced a definite change of condition, does the visible reaction of the separation of white drops of sulphur occur.

* As was to be expected (p. 257), the separated sulphur is at first amorphous; it has, however, other properties from the amorphous sulphur prepared by sudden cooling.

The best known thiosulphate and the one most used, is that of sodium, $Na_2S_2O_3$. It is prepared in large quantities, partly by the method given, chiefly, however, from the waste products obtained in the manufacture of coal-gas, in a manner which cannot be here explained.

The application of the thiosulphates depends partly on its solvent power for the salts of heavy metals, which will be explained later (*vide* Chaps. XXXV. and XLIII.), and partly on the fact that it is a reducing agent. By chlorine it is first oxidised to sulphate and sulphur—

$$Na_2S_2O_3 + Cl_2 + H_2O = Na_2SO_4 + 2HCl + S.$$

An excess of chlorine also converts the sulphur to sulphuric acid—

$$S + 3Cl_2 + 4H_2O = H_2SO_4 + 6HCl.$$

A large quantity of free chlorine, therefore, can be destroyed, *i.e.* converted into hydrogen chloride, by this salt. It is therefore used to remove the excess of chlorine from fibres and textile fabrics bleached by it, since such excess would have a destructive action. By reason of this application it has received the name *antichlor*.

* The products of oxidation of the thiosulphate, and any excess of the latter, are removed from the woven and spun materials by the efficient washing which is necessary. In the case of the dechlorination of bleached paper fibre, however, an excess of the salt generally remains behind, and hence many kinds of writing paper and pasteboard contain sodium thiosulphate. A knowledge of this fact is of importance in some cases.

Thiosulphate undergoes another kind of oxidation by means of free iodine. The process takes place according to the scheme

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI,$$

or, if we write the ions,

$$2S_2O_3'' + I_2 = S_4O_6'' + 2I'.$$

There is produced, therefore, not sulphate, but a new salt with the divalent ion S_4O_6''. The corresponding acid is called *tetrathionic acid*. This acid will be discussed at a later point along with related substances; at present we are interested in the transformation of the thiosulphate.

The process takes place with great quickness and sharpness, and on it, therefore, a splendid method of volumetric analysis can be based. In the first place, free iodine can be determined by means of a titrated solution of sodium thiosulphate. Further, the method can be used to determine the amount of all substances which liberate a proportionate amount of iodine from potassium iodide, *e.g.* chlorine or bromine. Finally, it can be employed for the determination of all substances which bind free iodine, by allowing these to act on a known excess of iodine dissolved in potassium iodide and titrating the residue with thiosulphate.

The value of the method depends not only on the variety of its applications but also, very materially, on the fact that an aqueous solution of thiosulphate, although it is a powerful reducing agent, is not, or rather, is only exceedingly slowly, oxidised by the free oxygen of the air. One could, of course, perform the analyses just described with sodium sulphite in place of thiosulphate, but, in this case, there is the difficulty produced by the great liability of this solution to change in the air, which makes the task less convenient and therefore less exact.

As can be seen from an examination of the equation $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$, or $2S_2O_3'' + I_2 = S_4O_6'' + 2I'$, neither hydrion nor hydroxidion is produced or used up in the reaction between iodine and sodium thiosulphate. That is to say, the solution remains neutral, if it was previously neutral, or, if it was previously acid, it retains its degree of acidity.[1] It is of importance that one should pay attention to this fact, since it occasionally finds application in analysis.

Polythionic Acids.—Further, sulphur forms, with hydrogen and oxygen, a series of dibasic acids which show a certain amount of agreement in their composition, and have therefore received similar names. These are:—

Dithionic acid, $H_2S_2O_6$.	Tetrathionic acid, $H_2S_4O_6$.
Trithionic acid, $H_2S_3O_6$.	Pentathionic acid, $H_2S_5O_6$.

For every two atoms of hydrogen and six of oxygen, these acids contain from two to five atoms of sulphur. In the names of the acids the latter numbers are expressed by the Greek numerals.

All the "polythionic acids," as they are collectively called, are readily decomposable substances, which are known only in dilute aqueous solution or in their salts, but not in the free state. On standing some time they undergo decomposition in solution in accordance with the equation

$$H_2S_mO_6 + H_2O = H_2SO_3 + H_2SO_4 + (m - 2)S,$$

that is to say, they yield sulphurous and sulphuric acids and sulphur. Only dithionic acid gives the first two substances alone, without separation of sulphur. These reactions take place with the aqueous solutions both of the free acid and of the salts. At the ordinary temperature, however, the velocity is not great; in the second case, it is practically zero. The reaction, however, can be completed in a few moments by a suitable elevation of temperature. The salts thereby pass into sulphates, whereas sulphur dioxide escapes, and, as the case may be, sulphur separates out. This occurs in accordance with the equation

$$Na_2S_mO_6 = Na_2SO_4 + SO_2 + (m - 2)S,$$

where the sodium salt is taken as an example.

Dithionic Acid.—The preparation of the above acids varies from case to case. *Dithionic acid*, or *hyposulphuric acid*, as it was formerly called, is obtained in the form of its manganese salt by passing sulphur dioxide into cold water in which finely powdered manganese dioxide is suspended. Whereas, at higher temperatures, only manganese sulphate is hereby formed ($MnO_2 + SO_2 = MnSO_4$), by careful action at lower temperatures, manganese dithionate is formed, in accordance with the equation

$$MnO_2 + 2SO_2 = MnS_2O_6.$$

The salt is soluble in water, and the progress of the reaction can be followed by means of the gradual disappearance of the dark grey manganese peroxide.

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[1] The liquid cannot be alkaline, because free iodine cannot exist along with alkali.

To obtain the free acid from the manganese salt, barium hydroxide is added to the solution. Manganese hydroxide is precipitated, and by evaporating the solution and crystallisation, the barium salt of dithionic acid can be obtained pure.[1] On decomposing a solution of this salt with dilute sulphuric acid, difficultly soluble barium sulphate is precipitated (p. 290), and free *dithionic acid* remains in solution.

* When, as in the present case, different products can be formed from given substances, those which are least stable are first formed. This important and general law has already been discussed in the case of the action of chlorine on solutions of caustic soda; the present case is another example of the law. If it were not for the action of this law, we should have no opportunity of becoming acquainted with unstable compounds.

The aqueous solution of dithionic acid has a strong acid taste and reaction. On attempting to concentrate it by evaporation, it very soon begins to smell of sulphur dioxide, and at the same time it contains sulphuric acid. The decomposition of this acid takes place in accordance with the equation

$$H_2S_2O_6 + H_2O = H_2SO_3 + H_2SO_4,$$

and all the more quickly the more concentrated the solution. A characteristic precipitant for dithionic acid, or better, for the ion S_2O_6'', is not known, since all its salts are soluble. Its identification and determination depend on its transformation into sulphurous and sulphuric acids, *without* separation of sulphur.

Trithionic Acid.—Salts of this acid are obtained by various reactions, the most readily understood of which is the action of sulphur dichloride (p. 301) on sodium sulphite—

$$2Na_2SO_3 + SCl_2 = Na_2S_3O_6 + 2NaCl.$$

In dilute aqueous solution this acid is also little known, since it very quickly undergoes decomposition into sulphurous and sulphuric acids and sulphur—

$$H_2S_3O_6 + H_2O = H_2SO_3 + H_2SO_4 + S.$$

Here, also, we have the case that the ion S_3O_6'' is fairly stable in neutral solution, *i.e.* in the absence of hydrion, whereas it immediately undergoes decomposition in the presence of the latter. The reason of this is again to be sought for in the fact that in the second case more stable compounds can be formed, for whose formation hydrion is required.

Tetrathionic Acid.—The formation of the ion of this acid in the action of iodine on sodium thiosulphate, has already been described (p. 297). For the purpose of preparing the free acid, the lead salt of thiosulphuric acid is used. This is decomposed with the calculated quantity of iodine according to the equation

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[1] In this reaction, some sulphate is always formed along with the dithionate. On treating with barium hydroxide, the former is precipitated as difficultly soluble barium sulphate, and the solution contains pure dithionate.

$$2PbS_2O_3 + 2I = PbS_4O_6 + PbI_2.$$

Exactly as in the corresponding reaction with the sodium salt, there are formed lead tetrathionate and lead iodide. The former passes into solution, the latter separates out. From the filtered solution, lead is precipitated as difficultly soluble lead sulphate by the careful addition of dilute sulphuric acid, while the tetrathionic acid remains in solution.

This solution has a strong acid taste and reaction, and is much less stable than that of dithionic acid. Sulphur soon separates from the solution, which simultaneously evolves sulphur dioxide and contains sulphuric acid. The decomposition ensues according to the equation

$$H_2S_4O_6 + H_2O = H_2SO_3 + H_2SO_4 + 2S.$$

Pentathionic Acid.—This is obtained by passing sulphuretted hydrogen into an aqueous solution of sulphurous acid. Whereas one portion of the substances simply undergoes transformation to sulphur and water, according to the equation

$$2H_2S + H_2SO_3 = 3S + 3H_2O,$$

another portion forms pentathionic acid and water, according to the equation

$$10H_2SO_3 + 5H_2S = 3H_2S_5O_6 + 12H_2O.$$

By filtration, a portion of the sulphur can be separated. The other portion, however, is present in such a fine state of division that it behaves almost like a dissolved substance, and is not retained by a filter. By preparing a salt of pentathionic acid from this solution, recrystallisation, etc., pure compounds of pentathionic acid can be obtained. We shall, however, not enter here on a description of the very troublesome methods by which this object is attained.

Pentathionic acid is also unstable, and readily decomposes into sulphurous acid, sulphuric acid, and sulphur.

Solutions containing one of the higher polythionates soon undergo transformation in such a way that other thionates are produced. Thus, *e.g.*, the trithionate passes into dithionate and tetrathionate. For the sodium salts, the equation is simply $2Na_2S_3O_6 = Na_2S_2O_6 + Na_2S_4O_6$; similarly for the other salts. It is, therefore, very difficult to obtain these compounds in the pure state.

G. *Halogen Compounds of Sulphur*

Chlorides of Sulphur.—If a current of dry chlorine be passed over sulphur gently warmed in a retort, a red-brown liquid is formed, which distils over at 138° and has a very unpleasant smell. This is a chlorine compound of sulphur; its composition is expressed by S_2Cl_2, and it is called *sulphur monochloride.*

Sulphur monochloride is a solvent for sulphur, of which it dissolves large quantities. The more volatile monochloride can be again separated from the less volatile sulphur by distillation. The monochloride is decomposed in moist air, and, in general, by water; the chlorine is converted into hydrochloric acid, while the sulphur partly separates out as such, and partly forms sulphurous and thiosulphuric acids. The relative amounts of these two vary regularly with the amount of water, and the process can, therefore, not be represented by an equation with definite coefficients.

Sulphur monochloride is employed in the arts for vulcanising caoutchouc. By the absorption of sulphur the latter becomes more elastic and resists changes of temperature better.

If more chlorine is passed into sulphur monochloride, it is absorbed; in varying amounts, however, depending on the temperature and pressure. From the investigations made on this point there are indications that two compounds of the formulæ SCl_2 and SCl_4 are formed. These investigations, however, require to be revised from the point of view of the theory of chemical equilibrium before definite conclusions can be drawn from them. The substances formed in the way described are scarcely to be distinguished by their appearance from sulphur monochloride. Since, however, they give off chlorine, the smell of this element is perceived along with that of the compound.

Chlorides of Sulphuric Acid.—On neutralising a base with hydrochloric acid, the chloride of the metal present is formed along with water, in accordance with the equation $MOH + HCl = MCl + H_2O$. This process may be regarded, formally, as if hydroxyl were replaced by chlorine, and we may ask if other hydroxyl compounds cannot experience a similar replacement.

In sulphuric acid, now, as in all oxygen acids, the hydrogen can be assumed to be united to oxygen to form hydroxyl. The suitability of this assumption is seen from the fact that the actual reactions of this substance are in agreement with it.

Thus, in fact, derivatives of sulphuric acid are known which have the same relation to it as the metal chlorides have to the metal hydroxides, and which, therefore, support the assumption that in sulphuric acid hydrogen and oxygen are united together to hydroxyl.

* A "proof" of this assumption is not given by those compounds. The actual phenomenon is that the elements O and H are eliminated in the proportions OH, and Cl simultaneously enters. It cannot

however, be asserted that these two elements, in order that they may be simultaneously eliminated, must previously have been united, for there are numerous cases in which such an assumption cannot be sustained. The sole purpose of this assumption, therefore, is to state that the reaction in question often and easily occurs.

* On such relations all the so-called "constitutional formulæ" of substances are based. These are a short expression for the chemical reactions actually observed. Since the latter, however, depend on other conditions besides the chemical nature of the substances,—*e.g.* on temperature, pressure, presence of other substances,—it is to be anticipated that a definite constitutional formula can represent the behaviour of the given substance only within a definite range, and will prove all the less satisfactory the more deeply and comprehensively the chemical behaviour of the substance is known.

* Such diversity can, if necessary, be expressed by the assumption of several constitutional formulæ; but this is only a makeshift. For the complete representation of the chemical behaviour, a numerical characterisation of the mutual relations of all the transformation products of the substance would be necessary. From such a standpoint, the chemistry of the present day is still very far removed.

If sulphuric acid be written as a hydroxyl compound, we obtain the formula $SO_2(OH)_2$ The atomic group SO_2 is called sulphuryl, and the two possible chlorine derivatives would have the following formulæ and names :—

$SO_2(OH)Cl$, Sulphuryl hydroxychloride,
SO_2Cl_2, Sulphuryl chloride.

The first name is not used, as being too long; the first compound, which still contains one acid hydrogen, is called chlorosulphonic acid.[1]

Chlorosulphonic acid is obtained from sulphur trioxide and hydrogen chloride, which combine on being gently heated—

$$SO_3 + HCl = SO_2(OH)Cl.$$

It forms a colourless liquid of density 1·7, and boils at 152°.

Chlorosulphonic acid fumes in moist air, because it undergoes transformation with the aqueous vapour to difficultly volatile sulphuric acid and hydrochloric acid—

$$SO_2(OH)Cl + H_2O = H_2SO_4 + HCl.$$

This reaction, viz., the re-formation of the original acid from its chloride by the action of water, is a general reaction of the acid chlorides.

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[1] The name is due to the fact that in organic chemistry numerous compounds of sulphuric acid are known of the formula $R . SO_2OH$ (where R is a compound "radicle") which are called sulphonic acids.

* In this respect the acid chlorides differ essentially from the metal chlorides, with which they have a *formal* similarity (p. 301). Whereas metallic hydroxides undergo transformation with hydrochloric acid to metallic chlorides and water, the acid chlorides, on the other hand, undergo transformation with water to hydroxide and hydrochloric acid. The reaction, $RCl + H_2O = R.OH + HCl$, proceeds in the first case from right to left, in the second case from left to right.

* If, now, we remember that, in principle, no chemical reaction can be complete, we can say that the two cases differ from one another essentially in the fact that the one or other side of the equation of reaction predominates. Or, as we can say with reference to what was set forth on p. 247, the acid chlorides undergo almost complete *hydrolysis* with water.

* While the previous remarks dealt with the reactions of the particular substances with a small amount of water, the processes which take place on solution in much water must also receive special consideration. Under these conditions, ion formation can occur, and, in general, *those reactions take place in which specially stable ions are formed.* Among these, chloridion must, in the first place, be reckoned.

On decomposing chlorosulphonic acid with much water, there occurs the reaction

$$SO_2(OH)Cl + H_2O = 2H^{\cdot}SO_4'' + H^{\cdot}Cl' = SO_4'' + Cl' + 3H^{\cdot},$$

i.e. the ions of sulphuric and hydrochloric acids are formed. Since these two acids are largely dissociated into ions, *i.e.* form very stable ions, this reaction is practically complete.

The capability of the acid corresponding to the chloride of forming stable ions will, therefore, increase the decomposability of the chloride by water.

In accordance with these considerations, it must be regarded as possible that hydroxides exist which stand between acids and bases in such a way that the two sides of the equation of reaction to some extent counterbalance one another. They will, therefore, under certain conditions, act as acids; under other conditions, as bases. We shall soon have an opportunity of indicating such substances (Chap. XIII.).

The second chloride of sulphuric acid, sulphuryl chloride, SO_2Cl_2, is produced by the direct combination of sulphur dioxide and chlorine. The reaction does not take place very quickly, but is greatly accelerated, catalytically, by the presence of camphor (an organic substance). It is obtained as a colourless, very mobile liquid, having the density 1·67 and boiling at 69°. The fact that the boiling point of sulphuryl chloride is so much lower than that of chlorosulphonic acid is an example of the general rule that the boiling point of the chlorine compounds is always considerably lower than that of the corresponding hydroxyl compounds. The same is seen on comparing chlorosulphonic acid (boiling point 152°) with sulphuric acid (boiling point 340°).

Sulphuryl chloride fumes only slightly in the air, because it reacts much more slowly with water than chlorosulphonic acid does. The latter compound is formed by the action of a small quantity of water—$SO_2Cl_2 + H_2O = SO_2(OH)Cl + HCl$; with much water, sulphuric and hydrochloric acids are formed—$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$.

* As the decomposition of sulphuryl chloride by much water takes place much more slowly than that of chlorosulphonic acid, it looks as if the former passed directly into sulphuric and hydrochloric acids without passing through the intermediate stage of chlorosulphonic acid. For the chlorosulphonic acid which is formed undergoes decomposition so quickly that at no time during the reaction can any considerable amount of it be detected.

* Similar relations are often found. In all cases, therefore, where existing intermediate stages are apparently passed over, it must be borne in mind that they may escape observation owing to differences in the velocity of reaction, as in the above case.

Besides the two chlorides of sulphuric acid, a chloride of pyrosulphuric acid—pyrosulphuryl chloride, $S_2O_5Cl_2$—is also known. It is obtained by withdrawing the elements of water (by means of phosphorus pentoxide) from chlorosulphonic acid, $2SO_2(OH)Cl - H_2O = S_2O_5Cl_2$. It is a liquid similar to chlorosulphonic acid, only more viscous and having a greater density. Its density is 1·82, and its boiling point 142°. Its vapour, on being heated, decomposes into sulphur trioxide, sulphur dioxide, and chlorine.

With water, pyrosulphuryl chloride reacts in a manner similar to the other chlorides of sulphuric acid. The reaction does not appear so violent as in the case of chlorosulphonic acid, because it takes place more slowly.

H. *Combining Weight of Sulphur*

Since sulphur forms a large number of compounds which can be analysed with exactness, very varying methods have been employed for the determination of this important combining weight. The most exact number was obtained by Stas by determining the ratio in which silver united with sulphur to form silver sulphide. On the other hand, by determining the amount of silver which can be obtained from a weighed quantity of silver sulphate, he obtained the data necessary for the independent calculation of the desired number.

For example, by heating 59·4225 gm. silver in sulphur vapour, 68·2482 gm. of silver sulphide were obtained: the two weights are in the ratio 1 : 1·1485. Further, 81·023 gm. silver sulphate yielded 56·071 gm. silver on being converted to this by heating in a current of hydrogen, in accordance with the equation $Ag_2SO_4 + H_2 = H_2SO_4 +$

2Ag. Since in silver sulphide, Ag_2S, the ratio of silver to sulphur is the same as in silver sulphate, there correspond to the amount of silver found, 64·3985 gm. silver plus sulphur, or 8·3275 gm. sulphur, and the remainder, 16·6245 gm., is oxygen. Since in silver sulphate there are four combining weights of oxygen to one of sulphur, we have the proportion $4 \times 16 : x = 16{\cdot}6245 : 8{\cdot}3275$, and $x = 32{\cdot}06$. The mean value of all such determinations has given the same number, $S = 32{\cdot}06$.

CHAPTER XIII

SELENIUM AND TELLURIUM

General.—Similarly to the triad chlorine, bromine, and iodine, the elements of the sulphur group also form a trinity of similar substances whose properties vary regularly with increasing combining weight The analogy of the combining weights is seen, in the first place, from the following table :—

Chlorine . .	35·45	Sulphur . .	32·06
Bromine . .	79·96	Selenium . .	79·1
Iodine . .	126·86	Tellurium . .	127·3

As can be seen, the combining weights of the corresponding members of the two groups are very nearly the same. Whereas, however sulphur and selenium have rather *smaller* values than chlorine and bromine, the relation is reversed in the case of iodine and tellurium.

A similarity also exists between the two groups in the fact that the first elements in each, chlorine and sulphur, occur very widely distributed in nature, while the other two pairs are relatively sparingly found. Further similarities will become apparent in describing selenium and tellurium.

Selenium was discovered in the year 1817 by Berzelius in the deposit of a sulphuric acid manufactory at Gripsholm. It is an element which, like sulphur, can exist in different allotropic forms Precipitated from aqueous solution, it is obtained as an amorphous red substance, and, with very dilute solutions, is got in the colloidal state i.e. it is apparently in solution and passes through a filter.

From comparatively concentrated solutions, selenium is obtained as a bright red precipitate which, even under the influence of the temperature of boiling water, cakes together to a dense, black-red mass. At 217° selenium melts and forms a dark, viscous liquid which solidifies on being quickly cooled, to an amorphous mass of a black-red colour which breaks with a conchoidal fracture. If this amorphous selenium be kept some time at a temperature of 100° to 150°, it becomes crystalline and grey, with a somewhat metallic lustre. At 650° it boils.

Whereas the amorphous selenium does not conduct the electric current to a measurable extent, the property of conductivity is possessed by the crystalline form.

* In this connection the special peculiarity is met with that the electrical conductivity of crystalline selenium depends on the illumination which it experiences. Its conductivity is all the greater the stronger the light which it receives. On altering the strength of the ight, these changes occur in an exceedingly short time. It has not et been determined on what this peculiarity depends, but it appears hat traces of foreign substances, more especially of the selenium comounds of the heavy metals which are mixed with selenium, play a great part. Nor is it possible to retain sensitive selenium preparations ermanently in a sensitive state. Its application in the arts, to which his property invites, is thereby, at present, greatly limited.

In its compounds, selenium greatly resembles sulphur, for seleniu-etted hydrogen, selenious acid, and selenic acid are not only similarly onstituted to the corresponding sulphur compounds, but, in part also, ave a similar behaviour. From the special description of the different ubstances, these similarities and differences will become apparent. he combining weight of selenium is Se = 79·1.

Seleniuretted Hydrogen, H_2Se.—Seleniuretted hydrogen is a olourless gas with a very unpleasant smell, recalling that of decaying dish. It is very poisonous, and calls for special care in working with . It readily dissolves in water in large amount. The solution has a ebly acid reaction, and in contact with the air red selenium quickly parates out, the hydrogen of the seleniuretted hydrogen combining ith the oxygen of the air to form water—$2H_2Se + O_2 = 2H_2O + 2Se$.

Seleniuretted hydrogen is the hydrogen acid of selenium in the me sense as sulphuretted hydrogen is the hydrogen acid of sulphur. he salts of seleniuretted hydrogen are the metallic selenides. By ason of the two combining weights of hydrogen, seleniuretted drogen is dibasic, and its salts, therefore, contain either two comning weights of a monovalent metal or one combining weight of a valent one, etc. Seleniuretted hydrogen can be obtained by the tion of stronger acids on metallic selenides. The method usually rsued is to prepare ferrous selenide, FeSe, by heating selenium with n filings, and to treat this with hydrochloric acid. In a manner rfectly analogous to the preparation of sulphuretted hydrogen (p. 0), ferrous chloride and seleniuretted hydrogen are formed in accordce with the equation

$$FeSe + 2HCl = H_2Se + FeCl_2.$$

From the solutions of the different heavy metals, seleniuretted drogen precipitates the corresponding selenium compounds as red or rk coloured substances. The compounds of selenium with sodium d similar metals are, however, readily soluble in water. In the air, these decompose similarly to seleniuretted hydrogen, so that after som time a red precipitate of elementary selenium is deposited from thei solutions. This property is made use of for the purpose of obtainin or of purifying selenium. The crude material is fused with sodiu hydroxide (or with sodium carbonate, which acts in a similar manner) and the filtered solution of the melt is exposed in shallow vessels t the air.

The poisonous action of seleniuretted hydrogen mentioned above depends essentially on its ready decomposability by oxygen. Seleniu thereby separates out in the tissues in a finely divided form, and act both chemically and mechanically as an irritant.

Isomorphism.—The selenium which separates out under th influence of the oxygen of the air on soluble metallic selenides i crystalline, and, on closer examination, it is found to exhibit the sam crystalline forms as monoclinic (prismatic) sulphur, which separate out from the fused mass. Further, elementary selenium occurs in som of the naturally occurring kinds of sulphur; it is mixed uniformly o combined with the sulphur, and imparts a rather dark, reddish colou to it. Lastly, a large number of corresponding compounds of the tw elements exist, having the same crystalline form and capable of forming homogeneous "mixed crystals," *i.e.* crystals the composition o which is not governed by the laws of stoichiometry, but which, lik that of solutions, can exhibit every relation within definite limits.

These facts are embraced under the conception of *isomorphis* (identity of form). In the first place, two substances are calle isomorphous when they have the same crystalline shape and can for mixed crystals. Thus sulphur and selenium are isomorphous i respect of their monoclinic forms; for both elements not only crysta lise separately in like shapes, but when they together pass into th solid state they form mixed crystals of varying composition, which i determined essentially by the relative amounts of the two elements i the mother liquor.

When one of the two isomorphous substances has the property crystallising in different forms, the other substance has often the sam property, and the different forms are alike in pairs. Thus it is to b expected that there should be a rhombic form of selenium correspon ing to the rhombic form of sulphur, for such a relationship is found i many other cases. Such a form of selenium, it is true, is not know but naturally occurring rhombic crystals of sulphur are found whic contain more or less selenium. Selenium is, therefore, capable of form ing mixed crystals with rhombic sulphur, and from this it may b concluded as probable that a rhombic form of selenium exists, althoug it is perhaps so little stable under the conditions hitherto employe that it has not yet been possible to observe it.

Elements which in the free state are isomorphous with o another, have the further peculiarity that their corresponding con pounds with other elements are usually isomorphous. Thus, for example, almost all the salts of sulphuric acid have the same crystalline forms as the corresponding salts (*i.e.* containing the same metals and having a similar formula) of selenic acid. Such relationships are often found, and they are also sometimes met with in cases where no isomorphism of the elements is known. Hence a wider conception of isomorphism has been developed, and the term *isomorphous in the wider sense* is applied to those elements which, while not themselves isomorphous, form isomorphous compounds of like constitution. Of this kind of isomorphism, also, several examples will be cited later.

Since isomorphism and similarity of constitution go hand in hand, the fact of isomorphism can be used in doubtful cases to obtain a clue to the formulation of the compounds of new elements, *i.e.* to the choice of the most suitable combining weight from among the possible multiples (p. 141). In former times, especially, the relationships of isomorphism were of great service in this direction.

* In drawing such conclusions, however, it is necessary to carefully satisfy oneself that isomorphism is really present. Identity of the crystalline system and the possibility of expressing the forms of the two substances by the same crystallographic constants within the error of experiment, are not sufficient for the purpose, since chance agreement could not be excluded in this way. A sure criterion of actual isomorphism is given if, along with the identity of shape, the property of forming mixed crystals can be demonstrated.

Selenious Acid.—When selenium is heated in the air or in pure oxygen, it takes fire and burns with a blue-white flame, forming selenium dioxide, SeO_2. At the ordinary temperature this compound, unlike sulphur dioxide, is not a gas, but a solid crystalline substance. Only on being heated does it volatilise, without melting, and pass into a vapour of the colour of chlorine.

Selenium dioxide, further, is formed by treating selenium with any oxidising agent. As a rule, it is obtained by heating selenium with nitric acid, evaporating to dryness, and subliming the residue.

Selenium dioxide dissolves in water and yields an acid liquid which contains selenious acid, H_2SeO_3. By evaporation, this compound can be obtained in transparent crystals which, on heating, lose water and pass into selenium dioxide.

Selenious acid is not a reducing agent like sulphurous acid. On he contrary, it readily gives up its oxygen, and elementary selenium eparates out. Thus, for example, it is reduced even by the organic matter which is usually present in the dust of the atmosphere, and, or this reason, the mouths of the vessels in which selenious acid is kept re generally covered with a crust of red selenium, and the preparaion itself assumes, in course of time, a reddish coloration.

The reduction of selenious acid to selenium takes place very easily nd smoothly by means of sulphurous acid, in accordance with the equation $H_2SeO_3 + 2H_2SO_3 = Se + 2H_2SO_4 + H_2O$. The selenium first separates out in the colloidal state, a red coloured, transparent liquid being formed. On standing some time, quickly if heated, selenium separates out as a brown-red precipitate. This phenomenon can be used for identifying selenious acid and its salts.

Selenic Acid.—Powerful oxidising agents are required in order to convert selenious acid to the highest stage of oxidation of selenium, viz. selenic acid. The sodium salt is obtained by fusing sodium selenite with sodium nitrate. The latter yields up one combining weight of oxygen, by which the former is oxidised: $Na_2SeO_3 + O = Na_2SeO_4$.

The free acid is most easily obtained by treating silver selenite with bromine. Silver bromide and selenic acid are formed in accordance with the equation $Ag_2SeO_3 + H_2O + Br_2 = H_2SeO_4 + 2AgBr$ In order to carry out this reaction, the silver salt is covered with water, and bromine added, with shaking, so long as its colour disappears.

The aqueous solution of selenic acid can be concentrated by evaporation, and a thickish liquid is finally obtained which has the density 2·6 and the general appearance of concentrated sulphuric acid. The pure acid solidifies to crystals which melt at 58°; the melting point is greatly lowered by quite small quantities of water. A crystalline hydrate, $H_2SeO_4 + H_2O$, melting at 25°, is also known.

Selenic acid is distinguished from sulphuric acid by its powerful oxidising action; it readily dissolves the noble metals and evolves chlorine with hydrochloric acid, thereby passing into selenious acid—$H_2SeO_4 + 2HCl = H_2SeO_3 + Cl_2 + H_2O$. The salts of selenic acid are isomorphous (p. 308) with those of sulphuric acid, and also exhibit similar solubility relations. For example, its barium salt is just as difficultly soluble as barium sulphate, and the salts of the two acids can, therefore, be readily confounded. In order to identify selenic acid in presence of sulphuric acid, the liquid is previously treated with a reducing agent. The former is thereby reduced to selenious acid or selenium, while the sulphuric acid remains unchanged, and can be determined as such.

Chlorine Compounds.—Of the remaining compounds of selenium, selenium tetrachloride has still to be mentioned. It is a white, crystalline substance with the formula $SeCl_4$, and is easily prepared by heating selenium in a current of chlorine. On being heated, it is converted into vapour without previous fusion. With water it forms selenious and hydrochloric acids, in accordance with the equation $SeCl_4 + 3H_2O = H_2SeO_3 + 4HCl$.

Compared with sulphur tetrachloride (p. 301), which is exceedingly easily decomposed, the corresponding selenium compound may be termed a very stable substance. This increase in the stability of the chlorine compounds forms a marked contrast to the decrease of the stability of the corresponding oxygen and hydrogen compounds.

Besides selenium tetrachloride there also exists a selenium monochloride, Se_2Cl_2, corresponding to sulphur monochloride. This is a dark red-brown liquid from which, when heated, selenium tetrachloride escapes while selenium remains behind—$2Se_2Cl_2 = 3Se + SeCl_4$. The stability relations are, therefore, different here from what they are in the case of sulphur, where the tetrachloride decomposes into chlorine and monochloride.

Tellurium.—While iodine is very similar to bromine, if not in external appearance, at least in the nature of the corresponding compounds, the differences between selenium and tellurium are more pronounced, so that it has repeatedly been regarded as doubtful whether these two elements ought to be regarded as members of the same family.

Tellurium is a greyish white substance with a metallic lustre; its density is 6·4, and it conducts the electric current like a metal. It melts at 450°, and boils at 1400°. The vapour is only slightly denser than corresponds to the formula Te_2.

The combining weight of tellurium, $Te = 127·3$, is, as has already been mentioned, greater than that of iodine, whereas the combining weights of the other elements of this group are smaller than those of the corresponding halogens. Many investigations have therefore been carried out because it was believed that this deviation was due to incorrect determinations; it has, however, been found with certainty that the numbers are as stated.

Besides the metallic tellurium, there is also a black, apparently amorphous form, in which tellurium is obtained by precipitation from its solutions. It has a considerably smaller density.

Tellurium combines with the metals to form tellurides; these correspond to the sulphides in composition, and have generally a metallic appearance. The tellurides of the alkali metals are soluble in water, and tellurium separates from these under the influence of the oxygen of the air.

Tellurium hydride, H_2Te, is obtained by the action of the strong acids on tellurides; it is a gas possessing an offensive smell and poisonous properties, behaves similarly to the hydrogen compounds of sulphur and selenium, and in aqueous solution is, like these, readily decomposed by the oxygen of the air.

Heated in the air, tellurium burns, forming the dioxide, which is a white substance volatile at a red heat. Tellurous acid, H_2TeO_3, is obtained by oxidising tellurium with nitric acid. It is a white mass, slightly soluble in water, and has only feebly acid properties. With strong acids, the compound behaves as a base, hydroxyl being eliminated and a salt formed. Compounds are hereby produced which are derived from a tetracid base, $Te(OH)_4 = H_2TeO_3 + H_2O$. These salts are, however, also very unstable towards water, just as, in fact, all substances which can act both as base and as acid yield in both cases only slightly stable compounds.

Tellurous acid can be converted into telluric acid, H_2TeO_4, by powerful oxidising agents. This has no similarity to sulphuric or selenic acid, for it forms a crystalline mass, difficultly soluble in water, and possessing feebly acid properties. The crystals which can be obtained from water have the composition $H_2TeO_4 + 2H_2O = Te(OH)_6$, and, on heating, pass first into the acid H_2TeO_4 and then into the anhydride TeO_3. The latter is a yellow mass, which is indifferent towards water.

Telluric acid also exhibits basic properties.

Whereas, therefore, the oxygen compounds of tellurium agree in composition with those of sulphur and selenium, their chemical behaviour is very different. It is, it is true, a general phenomenon that the elements with higher combining weight form more feebly acid or more strongly basic compounds compared with the related elements of lower combining weight, but it is seldom that the phenomenon makes its appearance so abruptly as in the present case.

Finally, it has to be mentioned that tellurium combines with chlorine to form the compounds $TeCl_2$ and $TeCl_4$, and with bromine to form $TeBr_2$ and $TeBr_4$. These are crystalline substances, volatile without decomposition at moderately high temperatures, and resembling in properties the halogen compounds of the metals, *e.g.* of mercury.

CHAPTER XIV

NITROGEN

General.—As was shown on p. 36, there is present in the air, besides oxygen, another substance which constitutes the greater part both by weight and by volume. From the fact that the residue of the air after removal of the oxygen can support neither combustion nor life, it was called *azote*, but it is now called *nitrogen*. Its chemical symbol is N, from nitrogenium. This name is due to the fact that nitrogen is an essential component of saltpetre (nitrum). Its combining weight is N = 14·04.

The properties of nitrogen are essentially those of the air minus those due to oxygen. Thus, it is colourless, odourless, and only slightly soluble in water. Its molar weight is 28; as gas, therefore, it has the formula N_2. It is distinguished from oxygen essentially by the fact that it is capable only in a very slight degree of reacting chemically with other substances. There are only very few substances which can unite directly with nitrogen. If, however, the nitrogen has once passed into combination, the substances which are formed show a very considerable variety and power of transformation, so that the range of nitrogen compounds is a large and important one.

Compounds of nitrogen are of frequent occurrence both in the mineral and, more especially, in the organic kingdoms. Of the former there may be mentioned the important groups of nitric acid and ammonia; these will presently be discussed in detail. In the organic kingdom, nitrogen is in so far of especial importance as the substances with which the phenomena of life are directly connected, and whose presence appears to be necessary for the processes of life, viz., the *albuminoids*, all contain nitrogen.

Preparation and Properties.—In order to obtain nitrogen, it is only necessary to free the ordinary air from the oxygen it contains. For this purpose, metals are most suitable which combine with oxygen and yield solid, non-volatile oxides. The choice is somewhat limited, from the fact that those metals which decompose water must be excluded. These would form hydrogen from the traces of water vapour present, and this would contaminate the nitrogen, and could be separated from it only with difficulty. The necessary conditions are best found united in *copper*.

If a current of air be passed through a tube filled with copper in the form of turnings or of thin wire, and raised to a medium red heat, it yields up all its oxygen to the copper and nitrogen escapes and can be collected over water (Fig. 89). A colourless gas is obtained, with which it is easy to demonstrate the property that burning substances, not only wood but also sulphur and phosphorus, are extinguished in it.

The density of the nitrogen so obtained is rather greater than that of nitrogen prepared from its compounds by chemical reactions. This, at first, puzzling phenomenon has been explained by the fact that besides nitrogen, there is present in the air a heavier gas which combines with copper just as little as nitrogen does, and therefore remains mixed with this. This was separated in the pure state from atmospheric nitrogen by Rayleigh and Ramsay in 1894, and has been found to be an elementary substance. It has been called *argon*.

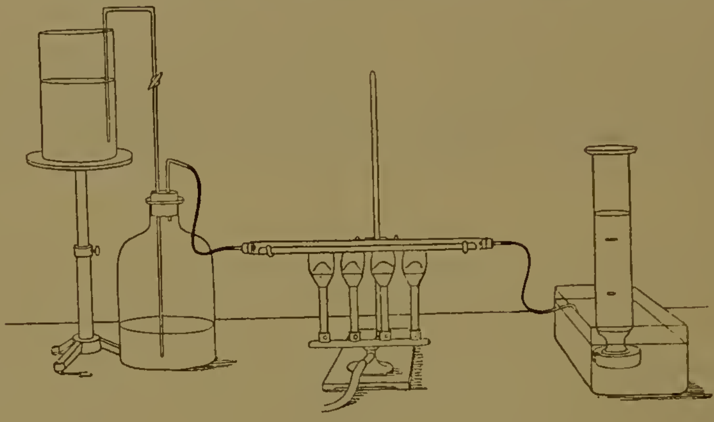

FIG. 89.

The density of pure nitrogen stands to that of oxygen very nearly in the ratio 7 : 8. Nitrogen is, therefore, the lighter component of the air, and, therefore, lighter than this itself.

At − 194°, nitrogen can be condensed under atmospheric pressure to a colourless liquid, which at − 214° passes into a solid, ice-like substance.

If the temperature is higher than − 146°, gaseous nitrogen cannot be made to assume the liquid state by any pressure; − 146° is, therefore, the *critical temperature* of this substance. The *critical pressure*, or the pressure at which, slightly below − 146°, condensation can still be effected, amounts to 35 atm.

Chemical criteria, by means of which gaseous nitrogen can be conveniently distinguished from other gases, scarcely exist. In general, one is content to regard as nitrogen, gases which are neither combustible nor support combustion, and which do not combine with metals.

phosphorus, and the other reagents for gases which are in use. Since, as has been mentioned, free nitrogen has little tendency to take part in chemical reactions, it is generally of no great importance whether nitrogen is present or not; it acts only as an indifferent diluent for the other gases with which it is associated.

If nitrogen, under a small pressure, is rendered luminous by an electric discharge in a tube arranged for that purpose (p. 96), a spectrum of numerous lines is observed which is more especially characterised by the appearance of bands shaded away on one side. These consist of numerous fine lines which, on the one side, are closely crowded together, and on the other side are regularly arranged farther and farther apart. By means of this phenomenon, the presence of nitrogen in gases can be recognised with comparative ease.

The Air.—Although the air by which we are surrounded is a mixture, it has to be taken into account in so many phenomena that a special discussion must be devoted to it here.

Air consists, in round numbers, of 0·21 parts of oxygen and 0·79 parts of nitrogen, by volume. If these volumes are multiplied by the densities of the two gases and divided by the sum of the two numbers, we obtain as the proportions by weight 0·23 and 0·77 respectively. The numbers are not perfectly constant, since processes are continually taking place in the air which tend to alter this ratio. Close investigation has, however, shown that the differences which actually occur move within very narrow limits about the mean values, oxygen 0·210, nitrogen 0·781, argon 0·009 parts by volume.

The influences which tend to alter the composition of the air consist, on the one hand, in the withdrawal of oxygen by oxidations of all kinds, *i.e.* by rapid and slow combustions. On the other hand, green plants have the property of giving off oxygen to the surrounding air, and the almost constant composition of the air which is observed is an expression of the fact that these two opposed actions exactly counterbalance one another.

If one considers now, that the processes by which oxygen is removed are concentrated in the large towns, where, conversely, the evolution of oxygen is very small, whereas, on the other hand, the evolution of oxygen by green plants occurs only in summer and during the day, one might expect much greater differences than actually occur. The cause of the equalisation is to be found in the great movements which the ocean of air constantly experiences. By reason of these, the one-sided actions do not take place on one and the same isolated portion of air, but are distributed over large and varying amounts which stream past over these different localities. These movements also produce an effective mixing of the different portions of the air, and the comparative constancy of the composition of the atmosphere is the result.

On account of the fact that the ratio of the volumes approximates to the round number 1 : 5, the supposition has sometimes been expressed that the air is a chemical compound of the two elements. This view is wrong, for the properties of the air are those which follow from the properties of its components on taking into account the proportions of mixing. A chemical compound, however, is characterised by the fact that its properties are essentially different from the corresponding mean values of the properties of its components.

For example, air alters in composition on being dissolved in water, since oxygen dissolves to a larger extent than nitrogen. The proportions in which the two elements are present in water saturated with air, are 0·35 oxygen to 0·65 nitrogen. Further, the components of the air can be separated by diffusion (p. 92), although not very successfully, since the two densities are fairly close to one another.

Besides the two gases mentioned, the air also contains as regular constituents water vapour, argon, and carbon dioxide. With regard to the first, the necessary data have already been given (p. 122) : the other substances will be discussed later.

The analysis of the air can be performed in many ways. The method described above (p. 314) can be developed to a quantitative one, as indicated in Fig. 89. This is done with greatest accuracy by bringing the air into a space shut off by mercury, measuring the pressure, temperature, and volume, and then removing the oxygen by means of a spiral of copper wire raised to a red heat by an electric current. After cooling, the three magnitudes are again determined, and by this means the volume relation is obtained. In Fig. 90 an apparatus constructed for this purpose is shown.

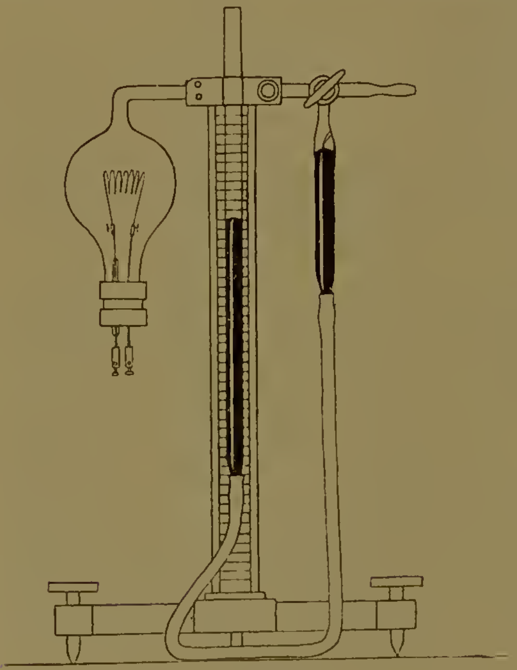
FIG. 90.

Instead of glowing copper, phosphorus can be used. This has the advantage that it removes the oxygen very completely from the air even at the ordinary temperature. The phosphorus is introduced in the form of thin rods into a glass apparatus of the form *A* (Fig. 91), which is also completely filled with water to the point *a*. The air to be investigated is measured in a graduated tube, the "gas burette" *B*, which is then united with the absorption pipette *A* by means of a narrow tube. By raising the pressure-tube *D* the air is forced over to the phosphorus. When the absorption of the oxygen is completed, the nitrogen is returned to the gas burette by the reverse process, and is there measured after the atmospheric pressure has been re-established by bringing the water levels in *B* and *D* to the same height.

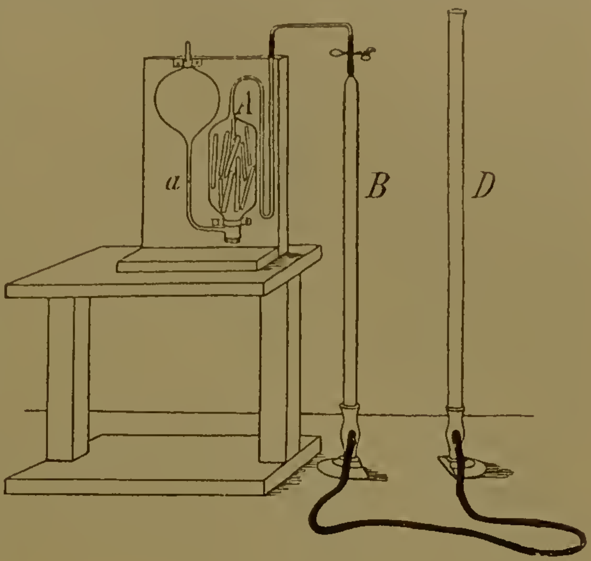

Fig. 91.

A third method, given more than a hundred years ago by Volta (the inventor of the voltaic pile), depends on the combination of oxygen with hydrogen. The air is placed over mercury in a graduated tube, into the upper end of which two platinum wires are fused; the volume, pressure, and temperature are measured, and hydrogen then added. By repeating the measurement, the total volume is ascertained. On allowing an electric spark to pass through the mixture, the oxygen combines with the hydrogen, and the former entirely disappears if sufficient hydrogen has been added. If the gaseous residue is now measured, $\frac{2}{3}$rds of the volume which has disappeared consists of hydrogen, $\frac{1}{3}$rd of oxygen. The amount of oxygen, by volume, in the air examined is, therefore, obtained by dividing the diminution of volume, after explosion, by 3.

Great importance was formerly attached to the determination of the amount of oxygen in the air, because it was believed that on it depended the good or ill health of man and beast. The fact, however, that the variations which occur are very small, and that the volume-concentration of the oxygen in the air is altered much more than the amount of these variations by the comparatively small changes in the pressure of the air at different times and at different heights, has led to the conviction that such influences are not appreciable; the analysis of the air has thereby lost much of its former interest.

Oxygen Compounds of Nitrogen.—The number of compounds which oxygen (partly along with hydrogen) is capable of forming with nitrogen, is very great. Instead of treating these strictly systematically according to their composition, it will be more expedient to first consider the most important and most widely distributed of them, from which the majority of the compounds are formed. These are *nitric acid* and its salts, the *nitrates*.

Nitric acid is an acid of the composition HNO_3. Its occurrence in the free state in nature is exceptional, for the reason that it is a strong acid, and, therefore, at once forms salts. All the more frequent and widely distributed are the salts of nitric acid, or the nitrates. *Saltpetre,* or potassium nitrate, KNO_3, has been known from ancient times, and occurs in the earth in places where nitrogenous animal substances, especially animal excremental matter, is subjected to the action of the atmospheric oxygen. It can be readily obtained by extracting the earth with water and evaporating the solution. Sodium nitrate, $NaNO_3$, known as *Chili saltpetre,* is found accumulated in the rainless districts of Chili, and serves as the most important source of nitric acid and of its derivatives. Finally, it has to be mentioned that the nitrogen, oxygen, and water in the air can, under the influence of electrical processes, combine to nitric acid, which is, therefore, not infrequently found in the form of its salts in rainwater, although in very small amounts.

Pure nitric acid, HNO_3, is obtained by distilling its salts with sulphuric acid. The corresponding sulphate is formed, and the nitric acid, which is readily volatile, can be distilled off from the non-volatile salts. With sodium nitrate, the reaction takes place according to the equation

$$2NaNO_3 + H_2SO_4 = 2HNO_3 + Na_2SO_4.$$

In this case, also, the process takes place in two stages; acid sodium sulphate is first formed (p. 289), $NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$, and the other reaction, $NaHSO_4 + NaNO_3 = Na_2SO_4 + HNO_3$, takes place only at higher temperatures. Since at the temperature necessary for this the nitric acid is unstable and decomposes into other substances, it is usual to take the components in accordance with the former partial reaction, nitric acid being obtained along with acid sodium sulphate. Likewise, it is customary to add a little water to the sulphuric acid, as aqueous nitric acid does not decompose nearly so readily when heated as the anhydrous acid.

* However, by carrying out the distillation in a rarefied atmosphere at a lower temperature (p. 157), the above disadvantages can be removed. In the manufactures, almost pure nitric acid is prepared on the large scale at the present day by distillation under reduced pressure.

Pure nitric acid is a colourless liquid, with a density 1·56, and boils at 86°. It does not keep well, for even under the influence of light, it decomposes into oxygen and lower (*i.e.* containing less oxygen) compounds of nitrogen, which dissolve with a yellow colour in the rest of the acid. Addition of water makes it much more stable. The cause of this is the same as that previously given in the case of perchloric acid (p. 219); nitric acid has a great tendency to form ions, and, therefore, processes by which water is produced from the acid, take place with especial readiness. This is what occurs in the decomposition of nitric acid under the influence of light, for the hydrogen of the acid thereby passes into water.

On adding increasing quantities of water to the acid, the boiling point of the latter rises not only to that of water but considerably higher. The highest boiling point, 120° under atmospheric pressure, is possessed by the 68 per cent acid. On further addition of water, the boiling point again sinks, and ultimately reaches that of water.

The relations which obtain here are therefore perfectly similar to those in the case of hydrochloric acid (p. 182). In this case also, the mixture of 0·68 nitric acid and 0·32 water, which corresponds, approximately, to the formula $2HNO_3 + 3H_2O$, must not be regarded as a chemical compound, for its composition changes with the pressure. In this case, indeed, the acid is all the more concentrated the higher the pressure under which the distillation proceeds.

The Chemical Properties of Nitric Acid.—The properties which are possessed by nitric acid, *as an acid*, must be distinguished from those which pertain to it in respect of other decompositions. The former depend, as has previously been explained (p. 242), essentially on the extent to which the acid contains hydrion; the others, however, depend on the composition and the stability of the anion, and of the undissociated acid.

With regard to the first point, nitric acid belongs to the strongest acids, and, in this respect, ranks along with hydrochloric acid. Accordingly, even at great dilution, it has an acid taste and reddens litmus. Likewise, it readily attacks and dissolves metals. In this case, however, hydrogen is frequently not liberated as such, but combines with the oxygen of the nitric acid to form water, corresponding reduction products being thereby formed.

Since the dissociation increases with dilution, the general acid properties of this substance will become most prominent in dilute solutions, whereas, on the other hand, the specific actions which have just been mentioned will be chiefly found in concentrated solutions.

As can be gathered from the statement made above, that pure nitric acid decomposes even under the influence of light, this substance belongs to the same type of compounds as ozone and hydrogen peroxide, viz. compounds which can give up oxygen and pass into more stable substances, and which, therefore, act as strong *oxidising agents.* As a matter of fact, this is the most prominent property of nitric acid, and most of its applications depend on it.

This property of nitric acid first became known in the case of its action on the metals. There are a number of metals, such as copper, mercury, and silver, which are not dissolved by dilute acids. On the other hand, they are precipitated from their salts by hydrogen. The cause of this lies in the very different conditions under which chemical equilibrium between the metals and hydrogen is established. Since a substance acts all the more strongly, *i.e.* has a greater tendency to disappear as such, the more concentrated it is, it can be imagined that all metals will be precipitated from their salts by hydrogen, i this is employed in suitable concentration. Such a reaction as $Zn + H_2SO_4 = ZnSO_4 + H_2$ could then be reversed, so that zinc and sulphuric acid would be produced from zinc sulphate and hydrogen.

The different metals, now, are distinguished by the differen concentrations of hydrogen required for such a reaction. Whereas in the case of zinc, it would require to be very great, since, indeed the decomposition of the acids by this metal takes place so easily, i would, on the other hand, be very small in the case of silver, for hydrogen, even under the ordinary pressure, and therefore of the correspondingly small concentration, is sufficient to precipitate silver in the metallic state from its salts. All the metals can, accordingly be arranged in a series, beginning with the metal which requires the greatest concentration of hydrogen for its precipitation, and ending with that which is in equilibrium with the most dilute hydrogen This series would be most naturally divided into two parts at tha point at which the concentration of the hydrogen corresponds exactly to one atmosphere. This is, it is true, an arbitrary choice, but i corresponds to by far the greatest number of cases in which the behaviour of the metals is tested or comes into question.

To the first division, that of the metals which evolve hydrogen belong, in the first place, all the light metals, and, of the heavy metals those belonging to the iron group. The heavy metals of the othe groups belong chiefly to the second division, but tin is an exception and lead stands on the border. These relations will be more fully discussed under the different metals.

Those metals, now, which are not dissolved by dilute acids with evolution of hydrogen, are, for the most part, readily dissolved by nitric acid. This is due to the fact that the nitric acid converts the hydrogen which is first formed in the action, although only in immeasurably minute traces, into water by oxidation, and remove it, therefore, from the sphere of action. In other words, its action is to maintain an exceedingly small concentration of hydrogen, and thereby make it possible for more of the metal to pass into solution.

There are also some metals, such as gold and platinum, which are not dissolved by nitric acid. This depends on the fact that even the small concentration of hydrogen obtained by means of nitric acid, is too great to allow of a reaction taking place in the sense of a displacement of hydrogen. In order to dissolve such metals, stronger oxidising agents are required, by which a still smaller concentration o hydrogen is achieved.[1]

This peculiarity of nitric acid of dissolving silver but of leaving gold unattacked, is used for the separation of mixtures or alloys of the two metals; on treatment with nitric acid the silver passes into solution, whereas the gold remains undissolved. On account of its solvent power, this acid was called *aqua fortis* by the alchemists.

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[1] Solution is also obtained with more feeble oxidising agents, provided the *produc formed* is particularly stable. We shall enter into this at a later time.

* Those metals which, like zinc and magnesium, dissolve in dilute acids with evolution of hydrogen, are also dissolved by nitric acid. In spite of the fact that they are dissolved, the evolution of hydrogen in these cases appears greatly diminished. This also is due to the fact that the hydrogen combines with the oxygen of the nitric acid to form water; in this case, however, the removal of oxygen goes further, and, in place of the brown, gaseous products of reduction, compounds of nitrogen are formed which contain hydrogen. These have basic properties, and remain, therefore, dissolved in the acid liquid, with formation of salts. The last product of this reaction is ammonia, which will be discussed further on.

The Salts of Nitric Acid.—Nitric acid is a monobasic acid, and forms only one class of salts, namely, monovalent metals give salts of the formula MNO_3, divalent metals, salts of the formula $M(NO_3)_2$, etc. These salts can be formed in all the ways we have got to know in which salts are formed, for example, by the action of nitric acid on bases or hydroxides.

The nitrates all have the property of being more or less readily soluble in water, so that no precipitation reaction is known for the ion NO_3'. By reason of the large amount of oxygen they contain, the salts detonate when thrown on incandescent charcoal, *i.e.* the charcoal undergoes, at the expense of the oxygen of the nitrate, rapid combustion combined with vivid production of light. The oxygen is liberated by the heat, for although the nitrates are much more stable than nitric acid, they all exhibit the property of decomposing at moderately high temperatures with evolution of oxygen, the metal thereby generally remaining behind as oxide.

The most important applications of the nitrates, also, depend on the readiness with which they give up oxygen. These will be mentioned in describing the salts under the respective metals.

The identification, also, of nitric acid and of the nitrates depends on their oxidising action. If a liquid containing a nitrate is warmed with some copper and sulphuric acid, the copper is oxidised, and the products of the reduction of the nitric acid are evolved as brown fumes, which are readily recognised. Smaller quantities of NO_3' can be detected by colouring the acid liquid to be investigated with some indigo, and heating. Indigo is a dye which can be recognised even in very small quantities by its pure blue colour, and which is readily oxidised to colourless or yellowish coloured products. If, therefore, the acidified blue liquid becomes colourless when heated, the presence of nitric acid can be conjectured. The test is, however, not unequivocal, since other oxidising agents (*e.g.* chloric acid) also decolorise indigo.

An unmistakable test consists in the dark coloration produced by iron salts in liquids containing nitrates. The theory and practical details of this reaction will be given somewhat later in connection with the compound here in question, viz. nitric oxide.

Nitrogen Pentoxide.—If pure nitric acid be treated with dehydrating agents, it loses the elements of water and passes into its anhydride (p. 210), in accordance with the equation

$$2HNO_3 - H_2O = N_2O_5.$$

To effect this reaction it is not sufficient to use sulphuric acid, but the most powerful desiccating agent known, viz. phosphorus pentoxide, must be employed. This substance, which we shall soon describe more fully, is a white, snow-like powder, obtained by burning phosphorus in dry air. If this is added to nitric acid contained in a retort, and the mixture distilled after some time, the anhydride of nitric acid passes over as a mobile, very volatile liquid, which soon solidifies to a white, crystalline substance, melting at 30°. This is exceedingly unstable, and decomposes spontaneously into oxygen and nitrogen peroxide: $2N_2O_5 = 4NO_2 + O_2$. The decomposition, also, is not prevented by sealing up the substance in tubes and thus protecting it from the action of the air; such tubes usually explode after some time, when the pressure of the gaseous products of decomposition has become great enough.

Nitrogen pentoxide dissolves in water, with formation of nitric acid, the process expressed in the above equation taking place in the reverse sense.

* **Thermochemical.**—The heat of formation of solid nitrogen pentoxide is 55 *kj*, that of the gaseous, zero. On dissolving in water, 70 *kj* are developed, two moles of dilute nitric acid being thereby produced. We have, therefore, the equation $2N_2 + 5O_2 + aq. = 4HNO_3 aq. + 2 \times 125$ *kj*. If it is desired to refer the heat of formation of nitric acid to the elements hydrogen, oxygen, and nitrogen, the heat of formation of water, $2H_2 + O_2 = 2H_2O + 2 \times 286$ *kj*, has to be added, and there is obtained

$$H_2 + N_2 + 3O_2 + aq. = 2HNO_3 aq. + 411 \ kj.$$

The heat of formation of one mole of dilute nitric acid from hydrogen, nitrogen, oxygen, and water, is, therefore, 205 *kj*.

Nitric Oxide.—Lower oxides of nitrogen are formed by the action of nitric acid on copper or other metals. The nature of this reaction has already been explained; it depends on the fact that the hydrogen of the nitric acid which is replaced by the metal combines with the oxygen of another portion to form water. Various products of reduction are here formed, according to the metals, the temperature, and the concentration of the acid employed. Of these compounds, nitric oxide can be most easily prepared pure. The equation according to which it is formed is

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

In explanation it should be remarked that copper is divalent (p. 152), and therefore occupies the place of two combining weights of hydrogen in nitric acid. Copper nitrate, which is formed in this reaction, has, therefore, the formula $Cu(NO_3)_2$.

The preparation is carried out by allowing not too concentrated nitric acid to act on copper wire or chippings. Brown coloured gases are evolved, which become colourless on being passed through water, and then consist of nitric oxide. The molar weight of this gas amounts to 30, in agreement with the formula given, NO.

Nitric oxide is dissolved only slightly by water, and, in its physical properties, behaves quite similarly to the so-called permanent gases, oxygen, hydrogen, and nitrogen. Under the ordinary pressure, it does not liquefy till − 154°, and its critical temperature is − 93°.

The most conspicuous property of this compound is its power of combining at the ordinary temperature with oxygen. If a cylinder filled with nitric oxide is opened in the air, its contents at once become brown, since the gas absorbs oxygen and passes into the compound NO_2, which is coloured brown. If pure oxygen be passed into nitric oxide standing over water, the volume, instead of increasing, diminishes, and by careful addition of oxygen, all the gas can be made to disappear. This is due to the fact that the compound formed, NO_2, is dissolved by the water.

Formerly, attempts were made to employ this reaction for the analysis of the air, by mixing this with a measured amount of "nitrous air" and determining the diminution of volume. The process, however, varies somewhat according to circumstances, so that the analysis by this method cannot be made sufficiently exact.

Nitric oxide readily dissolves in solutions of *ferrous salts*, with production of a dark, brown-violet coloration. This phenomenon, the explanation of which cannot be given till later (Chap. XXVII.), serves as a convenient aid to the detection, not only of nitric oxide, but also of all the other oxygen compounds of nitrogen, which are first converted into nitric oxide by the iron salt employed (usually ferrous sulphate). On heating to boiling, the dark brown iron compound decomposes again into the iron salt used and nitric oxide, which escapes. In this way pure nitric oxide can be prepared by absorbing the impure gas by means of a ferrous salt, and then expelling it from the solution by heat. The other gases are either not absorbed, or they are not given off on heating.

* In making use of this phenomenon as a *reaction for the detection of the oxygen compounds of nitrogen*, the substance to be tested is

dissolved in a small quantity of concentrated sulphuric acid. To this a solution of ferrous sulphate is added, care being taken that it does not mix with the acid, but forms a layer above it; the great difference in density makes this easy to do. If an oxygen compound of nitrogen is present, a dark layer is formed after some time between the two liquids, and has the appearance of a dark band when viewed from the side (Fig. 92).

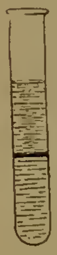


Fig. 92.

Nitric oxide decomposes fairly readily into oxygen and nitrogen. For this reason, phosphorus burns in this gas with a bright flame in a manner similar to what it does in oxygen. All the same, the oxygen is not present here in the free state, and in the case of feeble actions at a lower temperature, the oxygen is not separated with sufficient rapidity to maintain the combustion. Thus glowing charcoal and burning sulphur are extinguished in nitric oxide, whereas brightly burning wood continues to burn. Its heat of formation is − 90 *kj*; a considerable amount of heat, therefore, is developed in its decomposition.

Nitrogen Peroxide.—The brown gas which is immediately formed by the combination of oxygen with nitric oxide contains twice as much oxygen as the latter. By means of a freezing mixture it can be easily condensed to a liquid of a yellow-red colour, the colour of which is all the feebler the lower the temperature. If the temperature is sufficiently low, the liquid solidifies to almost colourless crystals which melt at − 12°. At 22°, the liquid boils.

In accordance with what has been said, the formula of the compound is NO_2, or a multiple of this. On attempting to obtain information on this point from the vapour density, values are obtained for the molar weight which vary with pressure and temperature. The lower the temperature and the higher the pressure, the more nearly does the molar weight approach the value 92; on the other hand, on raising the temperature and diminishing the pressure, the numbers approach the value 46. At 100° the value 46 is reached even under a pressure of 2·3 cm., and on further diminution of the pressure remains constant

At the same time, the colour of the vapour changes. Whereas at comparatively low temperatures a medium yellow-brown colour is to be observed, the coloration becomes darker and darker red-brown the more one passes into the region of small vapour density, and, finally, the vapour is black-red and almost opaque even in thin layers. On lowering the temperature and increasing the pressure, the former pale colour returns

* These relations can be easily made clear by filling two similar tubes of about 2 cm. diameter with the vapour of nitrogen peroxide under the same conditions, sealing them off, and heating one of them. Whereas the tube which is kept at the ordinary temperature appears pale brown in colour, the heated one soon acquires a pronounced dark

colour. The comparability of the two tubes is assured by the fact that, under these conditions, both contain the same amount of substance independent of the temperature.

These phenomena are explained by the fact that there are two different compounds of the same composition, which are polymeric, the one containing twice as many combining weights of the two components as the other. In accordance with the density, the former has the formula NO_2, the other N_2O_4. The former is dark coloured, and is formed at a high temperature and under a small pressure; the latter is almost colourless, and is formed from the former under the opposite conditions. Under all circumstances, the vapour of nitrogen peroxide is a mixture of the two forms, and the relative amounts of these can be calculated from the density of the vapour.

* Thus, at 50° and 49·8 cm. pressure, the molar weight D has been found equal to 62. If x be the fraction of the total amount by volume formed by NO_2, that formed by N_2O_4 is equal to $1-x$, and a mixture of the two has a molar weight $D = 46x + (1-x)92$. Hence, $x = \frac{92 - D}{46}$, from which, substituting the value of $D = 62$, $x = 0{\cdot}65$. Under the above conditions, therefore, the vapour contained 0·65 volumes of the simple compound and 0·35 volumes of the double compound. Since the weight of the latter is equal to 0·70 volumes of the simple one, the fractional amount of the simple compound by weight is $\frac{0{\cdot}65}{0{\cdot}65 + 0{\cdot}70} = 0{\cdot}48$.

There exists, therefore, between the two forms NO_2 and N_2O_4 a chemical equilibrium, in consequence of which the relative quantities of the two forms are determined by the temperature and pressure. If two of these magnitudes are given, the third is also fixed, *i.e.* at a given temperature and a given pressure only one definite ratio can exist between the two components. On the other hand, a perfectly definite temperature is required if it is desired to obtain under a given pressure a given ratio between the components.

The law which this equilibrium obeys is expressed by the formula

$$a^2/b = k,$$

where a denotes the concentration of the form NO_2, and b that of the form N_2O_4; k is a magnitude which is dependent on the temperature, but which, at constant temperature, is constant. It is, therefore, also called the equilibrium constant.

By concentration is understood the calculated amounts in moles of the substances present, divided by the volume measured in cc.

The above equation states that when the concentration of the two forms is diminished by increasing the total volume, the ratio of their amounts does not remain unchanged. For example, if the volume is so much increased that a diminishes to half its value, b must also diminish, not to half but to a fourth, in order that the equation may be fulfilled. In other words, on increasing the volume, *i.e.* diminishing the pressure, a portion of the form N_2O_4 must change into NO_2, as was stated above as the result of experiment.

If we reflect that by the change just mentioned of the more dense into the less dense form, the pressure must become greater than it would be if this change did not occur, we see that the formula stated above is a restatement of the law which was given in a qualitative form on p. 231; namely, when a system undergoes change, the process results which opposes this change. If the pressure is diminished, a portion of the denser gas decomposes and again partially cancels the diminution of pressure. On the other hand, if the volume is diminished, the pressure does not increase in the same proportion as in a single gas, but a portion of the NO_2 polymerises to N_2O_4, and the pressure cannot become so great.

Further, it has been established that heat is developed in the combination of NO_2 to N_2O_4. In accordance with the same principle, therefore, if the temperature be raised, that process will occur which opposes the rise of temperature, *i.e.* N_2O_4 will decompose into NO_2, because this process absorbs heat. This conclusion is also borne out by experiment.

* The heat of formation of nitrogen peroxide in its simple form NO_2 amounts to -32 *kj*; it therefore absorbs energy in its formation. In passing into the other form, N_2O_4, heat is developed: $2NO_2 = N_2O_4 + 54$ *kj*.

The Law of Mass Action.—The relationships which have just been set forth form a special case of a general law which governs all chemical states of equilibrium. It can be expressed in the following form.

Let a chemical reaction between $m_1, m_2, \ldots$ moles of the substances $A_1, A_2, \ldots$ and $n_1, n_2, \ldots$ moles of $B_1, B_2, \ldots$ be represented by an equation of the form

$$m_1A_1 + m_2A_2 + m_3A_3 + \ldots = n_1B_1 + n_2B_2 + n_3B_3 + \ldots,$$

then equilibrium will exist when the concentrations $a_1, a_2, a_3, \ldots b_1, b_2, b_3, \ldots$ of the reacting substances have acquired certain values. These values are given by the following equation:—

$$\frac{a_1^{m_1} \cdot a_2^{m_2} \cdot a_3^{m_3} \cdot \ldots}{b_1^{n_1} \cdot b_2^{n_2} \cdot b_3^{n_3} \ldots} = k.$$

The concentrations of the substances standing on the one side of the reaction equation, therefore, appear in the numerator, and those of the substances on the other side, in the denominator, of the fraction, and each concentration appears as a factor as many times as the number of the moles with which the particular substance takes part in the reaction. It is here presupposed that the reaction equation is written in molecular or molar formulæ. The magnitude k is constant at a given temperature, *i.e.* it is independent of the absolute value of the concentrations, but changes with the temperature.

Only gaseous and dissolved substances can have varying concentrations. In the case of solid substances and homogeneous liquids, the concentration changes so little with the pressure that its influence is scarcely appreciable. For this reason, in all cases where solid substances and homogeneous liquids take part in an equilibrium, the corresponding members occurring in the fraction on the left of the equation become constant, and can be brought over to the right-hand side, where they form all together a product which is constant for constant temperature.

This simple equation is the foundation of the whole theory of chemical equilibrium, and is applied in all cases where such questions have to be treated.

* As an example of its application, the more exact discussion of the case mentioned on p. 99 may be given; this deals with the chemical equilibrium between water vapour, iron, iron oxide, and hydrogen. The oxide of iron formed has the formula Fe_3O_4, and the equation, therefore, runs—

$$4H_2O + 3Fe = 4H_2 + Fe_3O_4,$$

and the equation of equilibrium—

$$a_1^4 a_2^3 / b_1^4 b_2 = k.$$

Here, however, a_2 and b_2 refer to solid substances (iron and iron oxide), and are, therefore, constant. On bringing them over to the right, there follows, $a_1^4/b_1^4 = b_2 k/a_2^3$, or, extracting the fourth root and putting the expression $\sqrt[4]{k b_2/a_2^3}$ equal to K, we obtain $a_1/b_1 = K$. That is to say, the ratio of the concentration (or the partial pressure) of the water vapour and the hydrogen must, at a given temperature, have a constant value, or, the two concentrations must be proportional. This is exactly what has been given by experiment.

The Influence of Temperature on Chemical Equilibrium.—The view is often found very wide-spread that at a very high temperature all chemical compounds must decompose into their components, and that at places, therefore, where such a temperature prevails, *e.g.* on the sun, the chemical elements can exist side by side only in the *uncombined* state.

On questioning experiment and the theory which has been developed on the basis of the general laws of energy, another answer is given by both. By applying the general principle of movable equilibrium, which states that whenever an equilibrium is compelled to change, processes occur which oppose the compelling force, we must say that at higher temperatures that reaction will occur which opposes the rise of temperature, *i.e.* which absorbs heat. If all chemical decompositions took place with absorption of heat, the view cited above would be correct. There are, however, numerous substances (and to these the oxygen compounds of nitrogen almost all belong) which are formed from their elements with absorption of energy. It is just at higher temperatures that such compounds become more stable, and they cannot, therefore, be decomposed by heat.

Numerous examples of this general law are known. Thus, the vapour pressure of every liquid increases with rise of temperature, *i.e.* more liquid evaporates into the given space because the evaporation takes place with absorption of heat. If a liquid should ever be found which passed into vapour with development of heat, it would also necessarily have the property that its vapour pressure would diminish with rise of temperature.

On considering the equation of equilibrium on p. 326 from this point of view, it can be said that, with a rise of temperature, those substances must increase which are formed with absorption of heat from the substances on the other side of the equation of reaction. From this it can always be seen in what sense a chemical equilibrium will be shifted with rise of temperature.

In the example cited above, heat is developed by the action of water vapour on iron; conversely, water vapour is formed from iron oxide and hydrogen with absorption of heat. Consequently, with a rise of temperature, the ratio of water vapour to hydrogen must increase, or, as the temperature rises, the decomposing action of the iron on water vapour becomes less and less. This result, also, was given by experiment before the theory was known.

This qualitative principle has also been brought into a form suitable for calculation. We shall, however, refrain from the deduction of this, as the qualitative form is sufficient for the applications which will be made of the principle.

The preparation of nitrogen peroxide can be carried out by means of the method already mentioned (p. 324), by converting nitric oxide into peroxide by means of free oxygen. The brown vapours obtained by the action of nitric acid on metals, after having been dried, are passed along with oxygen through a freezing mixture, the current of oxygen being so regulated that it is present in excess. The substance obtained can be easily purified by re-distillation.

For the preparation, also, use is made of the decomposition which some metallic nitrates undergo when heated. Lead nitrate, for example, gives nitrogen peroxide, according to the following equation :—

$$2Pb(NO_3)_2 = 4NO_2 + O_2 + 2PbO.$$

As has been already mentioned, the peroxide dissolves in water. In this process, however, it does not remain undecomposed, but reacts with the elements of water to form nitric and nitrous acids—

$$2NO_2 + H_2O = HNO_2 + HNO_3.$$

Nitrous Acid.—When nitrates, *e.g.* potassium nitrate, are treated with reducing substances, they lose oxygen and pass into the salts of another acid, known as *nitrous acid*. The new salts are called *nitrites*.

As reducing agent, metallic lead is chiefly used. This acts according to the equation

$$KNO_3 + Pb = KNO_2 + PbO.$$

By extracting with water, the readily soluble potassium nitrite can be separated from the difficultly soluble lead oxide. Small quantities of lead which pass into solution by reason of a side-reaction, are precipitated by passing in carbon dioxide.

On attempting to liberate the acid HNO_2 from the salt, it is found not to be stable in the free state. On pouring sulphuric acid over potassium nitrite, brown vapours are formed which, indeed, have the composition of an anhydride of nitrous acid, N_2O_3, but which prove to be a mixture of nitric oxide and nitrogen peroxide. If these vapours be passed into water, a feebly blue coloured solution is obtained, which probably contains some nitrous acid, but which constantly evolves nitric oxide and passes finally into nitric acid in accordance with the equation $3HNO_2 = 2NO + HNO_3 + H_2O$.

The same vapours are also obtained when nitric acid is decomposed with reducing agents under certain conditions. On heating nitric acid of density 1·30 – 1·35 with arsenic trioxide (p. 49), the latter takes up one combining weight of oxygen from the nitric acid, and the nitrous acid formed breaks up into water and the brown vapours mentioned. Since the latter are used in many important chemical reactions, especially in organic chemistry, this method of preparation is often used.

If these vapours are cooled in a freezing mixture, a liquid of a blue to green colour is obtained, and from this there can be separated by fractional distillation a portion of a dark blue colour, boiling at 3·5°, which, especially at low temperatures, appears pure blue. This has the composition of nitrogen trioxide or nitrous acid anhydride, and can be regarded as the compound N_2O_3.

For the detection of the ion NO_2' the general reaction for oxygen compounds of nitrogen by means of ferrous sulphate (p. 324), is, in the first place, employed. It is distinguished from the ion NO_3' of nitric acid by the fact that even on acidifying the salts of nitrous acid, or the nitrites, with any other stronger acids, the brown vapours are evolved the nature of which has just been given. By means of strong oxidising agents, NO_2' can be converted into NO_3'. A volumetric method depending on this will be given later on under potassium permanganate.

Further, the ion NO_2' unites with cobalt (p. 54) to form "complex" salts, some of which are readily recognised. This reaction, however, is much more used for the detection of cobalt than of nitrous acid, and will therefore be described under that metal.

The heat of formation of nitrous acid in dilute aqueous solution from its elements is − 28 *kj*, in accordance with the equation $H_2 + N_2 + 2O_2 + aq. = 2HNO_2\ aq. - 2 \times 28\ kj$.

Hyponitrous Acid.—By suitably regulating the reduction of the nitrates, a further amount of oxygen can be removed from them, and the *hyponitrites*, or the salts of *hyponitrous acid*, are obtained. Of the different methods of their preparation, the most easily understood, theoretically, is that by means of sodium. This metal is dissolved in mercury, and a solution of sodium nitrate or nitrite is treated with the "sodium amalgam" so obtained. Sodium amalgam acts much more moderately on other substances than pure sodium does, and is, therefore, better adapted than the latter for many preparations. The reaction can be formulated as follows:—

$$2NaNO_3 + 8Na + 4H_2O = Na_2N_2O_2 + 8NaOH,$$

when sodium nitrate is used, and

$$2NaNO_2 + 4Na + 2H_2O = Na_2N_2O_2 + 4NaOH,$$

when sodium nitrite is employed.

From the sodium salt, the difficultly soluble silver salt is prepared and purified by washing. On decomposing this salt with hydrogen chloride with exclusion of water, by using ether (an organic compound) as solvent, hyponitrous acid, $H_2N_2O_2$, is obtained in the form of white crystalline laminæ, which are very unstable and explode readily. The substance dissolves in water and yields a solution which keeps rather longer but which has also only a passing existence. It soon evolves a gas having the composition N_2O, which is the anhydride of hyponitrous acid.

The same substance, N_2O, which bears the name *nitrous oxide*, is produced in many cases in which hyponitrous acid ought really to be formed. It is very much more stable than the latter, and it has not yet been found possible to convert it back into hyponitrous acid or one of its salts.

Nitrous oxide is usually prepared by heating ammonium nitrate. With regard to this reaction, the reader is referred to the following section on the ammonia compounds; we shall here give the properties of the substance.

Nitrous oxide is a gas consisting of two combining weights of nitro gen to one of oxygen, to which, in accordance with the density 44, the formula N_2O has to be ascribed. It is colourless, has a faint, sweetish odour, and dissolves in water to a fairly large extent. At room temperature water absorbs about an equal volume of the gas. Likewise, the gas is comparatively easily liquefied, since its critical temperature lies at + 39°; the critical pressure amounts to 78 atm. At 0° the vapour pressure amounts to 36 atm., and the vapour pressure of one atmosphere is found at – 90°, which is, therefore, the ordinary boiling point.

Nitrous oxide parts with its oxygen still more readily than nitric oxide, so that not only phosphorus and brightly burning wood continue to burn in it, but also charcoal and sulphur, if previously sufficiently heated. Sulphur burning with a small flame, however, is extinguished when introduced into the gas.

Nitrous oxide is taken up by the blood and causes unconsciousness; it is therefore employed for obtaining transient narcosis.* The gas cannot be decomposed by the organism in such a way that its oxygen becomes available; if, therefore, nitrous oxide has to be inhaled for a lengthened period, it must be mixed with oxygen in the same proportions as the latter is present in the air.

In order to be formed from its elements, nitrous oxide would require to take up a large amount of energy, viz. 75 *kj*: $2N_2 + O_2 = 2N_2O - 2 \times 75\ kj$. In its decomposition, the same amount of energy is given out in the form of heat.

Nitro-compounds.—The acid actions of nitric acid depend on the fact that hydrion very readily splits off from the compound HNO_3. In view of the fact that other oxyacids, *e.g.* sulphuric acid, also give reactions in which hydroxyl acts in the place of hydrogen, the question must be asked whether, in the case of nitric acid, oxygen and hydrogen also act in common as hydroxyl.

From the fact of the strong electrolytic dissociation of nitric acid, it can, in the first place, be concluded that if such reactions are to occur, one will expect them to do so in the absence of water (which, of course, causes the formation of hydrion). This is, in fact, found to be the case.

In organic chemistry, a large number of compounds are known which are formed by the action of nitric acid on compounds containing hydrogen; the hydrogen from these, along with the hydroxyl from nitric acid, is eliminated as water, and the residual group NO_2 of the nitric acid unites with the residue of the organic substance, containing one combining weight less of hydrogen. The group NO_2 is called the *nitro-group*, and the compound RNO_2 formed in accordance with the general reaction equation $RH + HNO_3 = RNO_2 + H_2O$, is called a *nitro-compound*.

* In external appearance this process looks exactly like that of the formation of a salt, especially if the hydroxyl is assumed to be

present as such in the nitric acid, and the equation, therefore, be written in the form $NO_2OH + HR = R . NO_2 + H_2O$. It would, however, lead to mistakes if one were to estimate the significance of this apparent agreement so highly as to regard both reactions as essentially the same. For, the nitric acid would then have to be regarded as the base, and the hydrogen compound RH as the acid, in this reaction.

* The essential difference as compared with an ordinary salt formation consists just in the fact that we are in this case not dealing with an ion reaction as in the formation of a salt, for, neither is the compound RH an acid, nor the nitric acid a base, nor, finally, the nitro-compound formed a salt. According to what was said above, also, the difference becomes especially evident from the fact that the formation of nitro-compounds takes place all the more readily the more completely water is excluded, both the water originally present and that produced by the reaction itself. The latter can be rendered harmless by adding desiccating agents; and, as such, concentrated sulphuric acid is ordinarily employed. Nitration, or the preparation of a nitro-compound, is, therefore, usually carried out in the presence of larger or smaller amounts of concentrated sulphuric acid.

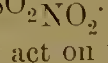
Nitro-compounds can be formed not only from nitric acid, with elimination of hydroxyl, but also from *nitrous* acid, with elimination of *hydrogen*. In order that such an elimination may take place, there must be present in the substance which is to pass into the nitro-compound, a part which will form a stable compound with the hydrogen. In most cases, this will be hydroxyl, which will give water with the hydrogen. We have then the equation.

$$R . OH + HNO_2 = R . NO_2 + H_2O.$$

* This equation has also only an apparent and no real resemblance to a salt formation. This is most clearly seen from the opposite rôle played by the groups NO_2 and R.

Lastly, nitro-compounds can be formed by the action of nitrogen peroxide on such substances as can directly form compounds by addition. The reaction corresponds to the formation of chlorides by the action of chlorine on substances of this class, *e.g.* metals.

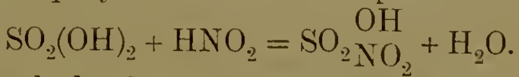
Whereas, in organic chemistry, numerous nitro-compounds are known, the number of inorganic nitro-compounds is comparatively small. Nevertheless, some of them are of sufficient importance to be discussed here.

Nitrosulphonic Acid.—The most important inorganic nitro-compound is nitrosulphonic or nitrosylsulphuric acid, the composition and reactions of which are expressed by the formula  $SO_2{}^{OH}_{NO_2}$.

In order to obtain such a compound, one must act on the hydrogen compound of the radical $SO_2(OH)$ with nitric acid, or on the hydroxyl compound of the same radical with nitrous acid. Both methods give the desired result.

The hydrogen compound of $SO_2(OH)$ is no other than sulphurous acid (p. 279); nitrosulphonic acid would, therefore, be formed from sulphurous acid and nitric acid.

As a matter of fact, this compound is obtained when, in place of sulphurous acid, its anhydride, sulphur dioxide, SO_2, is passed into concentrated nitric acid. This method has the especial advantage that no water is formed in the reaction, and the disturbances due to it are, therefore, not to be feared. The reaction takes place simply according to the equation $HNO_3 + SO_2 = SO_2\substack{OH\\NO_2}$.

The object is also attained by the other method. If nitrous acid (or its vapours, which have the same composition as it; p. 329) is introduced into the hydroxyl compound of the radical $SO_2(OH)$, *i.e.* into concentrated sulphuric acid, nitrosulphonic acid is formed along with water; the latter is taken up by the excess of sulphuric acid. The equation of this reaction is  $SO_2(OH)_2 + HNO_2 = SO_2\substack{OH\\NO_2} + H_2O$.

Besides these two typical methods, there are a number of others which can in principle be traced back to them. Some of these methods will be mentioned later.

Nitrosulphonic acid is a white, solid, crystalline substance, which melts, with decomposition, at 73°. It is very sensitive to water, and is transformed by it into sulphuric acid and nitrous acid (which, in turn, partially undergoes further decomposition; p. 329)—$SO_2(OH)NO_2 + H_2O = H_2SO_4 + HNO_2$. It dissolves, however, in concentrated sulphuric acid, and forms a very stable solution, which stands being diluted to some extent with water, corresponding equilibria being thereby established.

The compound also bears the name *leaden-chamber crystals*, for it is readily formed under the conditions prevailing in the lead chambers in the preparation of sulphuric acid, when too little water is present. By the addition of more steam, the leaden-chamber crystals, which are not formed in the well-regulated process, can easily be made to disappear.

Further, the retention of the valuable oxides of nitrogen in the waste gases from the sulphuric acid manufacture, which is effected by treating them with concentrated sulphuric acid in the "Gay-Lussac tower" (p. 286), depends on the formation of nitrosulphonic acid under these conditions. By mixing the solution of nitrosulphonic acid in excess of sulphuric acid with water, or dilute "chamber acid," the decomposition given above takes place, and nitrous acid is again evolved. This process takes place in the "Glover tower" before the entrance of the gases into the lead chambers (p. 285).

* It was also thought that a special rôle in the formation of sulphuric acid in the lead chamber had to be ascribed to the nitrosulphonic acid. For the present, however, this rôle is still so hypothetical, that no detailed description of it is required here.

Since one of the two combining weights of the hydrogen of sulphuric acid is still present unchanged in nitrosulphonic acid, it may be assumed that this will also have acid properties. Salts of this acid, however, are not known, and even in aqueous solution the acid cannot exist on account of the fact that it is decomposed by water.

* This decomposition can be looked upon as taking place in such a way that the acid HSO_3NO_2 first dissociates electrolytically, with formation of the anion SO_3NO_2'. This ion is not stable, but undergoes further decomposition with water, in accordance with the equation $SO_3NO_2' + H_2O = HSO_4' + HNO_2$. The two products of decomposition suffer, in turn, further transformations; the primary ion of sulphuric acid partially undergoes further decomposition into the secondary ion and hydrion, and the nitrous acid undergoes decomposition into nitric oxide and nitric acid, as described on p. 329.

* That nitrosulphonic acid is so sensitive to water, is due in this case, as in many others, to the fact that by the action of water very stable ions can be formed.

Other Nitro-compounds of Sulphuric Acid.—Just as one hydroxyl of sulphuric acid can be replaced by the nitro-group, the same ought also to be possible with the second, and the existence of a compound, dinitrosulphuryl, $SO_2(NO_2)_2$, might be expected. Such a compound would be formed, according to the general scheme, from sulphur dioxide and nitrogen peroxide, and could be regarded as quite similar to sulphuryl chloride, SO_2Cl_2 (p. 303). No such substance, however, is as yet known.

A dinitro-compound of pyrosulphuric acid, corresponding to pyrosulphuryl chloride, is, however, obtained by heating nitrosulphonic acid. This loses water and yields the former compound, in accordance with the equation $2SO_2(OH)(NO_2) - H_2O = S_2O_5(NO_2)_2$.

The same substance is obtained by the action of nitric oxide on sulphur trioxide, whereby sulphur dioxide escapes.

Dinitropyrosulphuryl is a white, crystalline mass, which looks like the leaden-chamber crystals, melts at 217°, and boils at 360°.

Aqua Regia.—By mixing nitric acid and hydrochloric acid a reagent is obtained which is used for dissolving certain metals, such as gold and platinum, which do not dissolve either in nitric acid or hydrochloric acid alone. On account of its solvent action on gold, it was called *aqua regia* by the alchemists.

The action of *aqua regia* depends, in the first place, on the fact that the hydrochloric acid is oxidised by the oxygen of the nitric acid to chlorine, which readily attacks the above metals and converts them into chlorides. Chlorine derivatives of the oxides of nitrogen, which will be presently mentioned, are also formed.

* An explanation is required why it is that *aqua regia* is a stronger oxidising agent than its components, especially nitric acid. From the fact that the latter has an oxidising action on hydrochloric acid and liberates chlorine, its free chemical energy cannot increase but only diminish.

* The explanation is found in the consideration that the chlorine compounds which are formed of the metals above-named have a much more stable character than the nitrates which would be formed by the action of nitric acid. The fall from the initial substance to the end-product is therefore greater in the case of *aqua regia* than in the case of nitric acid, not because *aqua regia* stands higher, but because the products of its action stand much lower.

On heating *aqua regia* alone, readily volatile substances, consisting of nitrogen, chlorine, and oxygen, and which are mixtures of different compounds, are evolved. Of these, the compounds nitryl chloride, NO_2Cl, and nitrosyl chloride, $NOCl$, are of interest. The properties of these are still somewhat doubtful, and will, therefore, not be given here. It should, however, be specially mentioned that they can be regarded as the chlorides of nitric and of nitrous acid, in which hydroxyl is replaced by chlorine. They are comparable, therefore, with the chlorides of sulphuric acid (p. 302).

Catalytic Actions of the Oxides of Nitrogen.—When nitric acid is employed for oxidation purposes, it is observed that, in general, the action is at first very feeble; it then increases, reaches a maximum, and again diminishes till it becomes inappreciable.

The last part of this process is readily intelligible. If one reflect hat in the oxidation process, both the concentration of the nitric acid and generally also of the substance to be oxidised, constantly diminishes, it must be concluded that the velocity of the process which rises and falls with the concentration of the reacting substances) must become smaller and smaller.

To what, then, is the initial acceleration due? One reason for it s found in the fact that the reaction takes place with strong development of heat; the temperature, therefore, rises, and since by reason f this the velocity of the reaction necessarily increases (p. 65), it is uite possible that the increase due to rise of temperature exceeds the iminution due to the consumption of the reacting substances.

If, however, the influence of the rise of temperature is excluded y continually conducting away the heat which is generated (*e.g.* by lacing the vessel in water at constant temperature), a very considerble initial acceleration is nevertheless still observed. This is due to he fact that the velocity with which nitric acid exercises its oxidising tion is catalytically accelerated to a very considerable extent by he presence of its products of reduction, more especially of nitrogen peroxide. The latter substance has already shown itself a very effective and important accelerator in the manufacture of sulphuric acid, *i.e.* in the oxidation of sulphurous acid by free oxygen (p. 286), and a number of other cases are also known in which it acts as an accelerator of oxidation.

In those cases, therefore, where it is desired to increase the oxidising action as much as possible, red, fuming nitric acid, *i.e.* an acid which contains lower oxides, especially nitrogen peroxide, in solution, is used. This acid is obtained by distilling nitric acid at a high temperature (p. 318), or, also, by adding a small quantity of a reducing substance (organic substance) during the distillation.

Conversely, in those cases where we are dealing with other actions of nitric acid in which oxidation has to be avoided, acid as free as possible from lower oxides must be used. This is recognised by its being colourless, and the lower oxides, which are more volatile than the nitric acid, can be removed from the yellow acid by passing a stream of dry air through it. This is of importance, for example, in the preparation of nitro-compounds from organic substances (p. 331).

Comparison of the Oxygen Compounds of Nitrogen with those of the Halogens.—Between the acids which are derived from nitrogen by addition of oxygen and the corresponding compounds of the halogens, there exists a striking similarity, which finds expression not only in the similarity of their formulæ, but also in the solubility and stability relations, and in the isomorphism of the corresponding salts. These similarities appear from the following summary:—

——	Perchloric acid, $HClO_4$
Nitric acid, HNO_3	Chloric acid, $HClO_3$
Nitrous acid, HNO_2	Chlorous acid, $HClO_2$
Hyponitrous acid, HNO	Hypochlorous acid, $HClO$
Nitrogen peroxide, NO_2	Chlorine peroxide, ClO_2
Nitric oxide, NO	——
Nitrous oxide, N_2O	Chlorine monoxide, Cl_2O

In both series, the stability increases as the amount of oxygen contained in the compound increases. In general, however, the chlorine compounds are less stable than the nitrogen ones.

The two chief compounds, chloric acid and nitric acid, form only soluble salts.

Ammonia.—Nitrogen and hydrogen can unite to form a compound containing three combining weights of hydrogen to one of nitrogen, and having, in agreement with the molar weight 17·1, the formula NH_3. It is a gaseous substance which dissolves readily in water, and has a pungent, very characteristic odour.

If nitrogen is mixed with hydrogen in the proportions of one volume to three, and an electric spark passed through the mixture, no explosive formation of the compound occurs. Nor does ammonia gas undergo explosive decomposition when it is heated, or when an electri spark is passed through it. In both cases, however, changes do take place; in the former, some ammonia is formed, in the latter, some is decomposed. If the action is continued for a fairly long time, the same condition is finally established in both cases, there being about 0·02 of the total amount present as ammonia, and the rest, 0·98, in the form of uncombined elements. This is, therefore, the chemical equilibrium which is established between the two substances under the above conditions, and which is produced by means of a reaction which proceeds with exceeding slowness.

If the ammonia is removed from the mixture in proportion as it is formed, the whole amount of gas can ultimately be made to combine. This occurs, for example, when the gases are kept in contact with an acid. Ammonia is taken up by acids, and if sparks are continued to be passed through the gas mixture while standing over an acid, all the gas will ultimately disappear.

As is apparent from the equation

$$N_2 + 3H_2 = 2NH_3,$$

the volume diminishes from 4 to 2, or to a half, when the elements pass into combination. The reverse change takes place when the gas is decomposed.

The change of energy occurring in the process is represented by the equation $N_2 + 3H_2 = 2NH_3 + 2 \times 50\ kj$.

Ammonia is absorbed in large amount by water, viz., about 800 volumes, or 0·6 part by weight, at room temperature. It, however, still follows Henry's law to some extent, especially at higher temperatures. It can be completely removed from the solution by boiling. From this it is apparent that all solutions of ammonia must necessarily have a lower boiling point than pure water. For if there were a solution with higher boiling point, this would remain behind during the distillation, and finally pass over unchanged in composition.

The aqueous solution of ammonia colours red litmus paper blue, and therefore contains a basic substance. Since in such substances hydroxidion, OH′, must be present, it must be assumed that in water ammonia has passed, at least partially, into a compound containing hydroxyl. This can occur only by it taking up the elements of water, and, therefore, a compound of the general formula $NH_3 + nH_2O$ is present. All known facts favour the view that $n = 1$, and that the compound must, therefore, be written $NH_3 + H_2O$, or, giving prominence to hydroxyl, NH_4OH.

Just as we recognised the compound ion of nitric acid, NO_3', to be similar to the simple ion Cl′ of hydrochloric acid, we also conclude that in the solution of ammonia there is present along with hydroxyl he compound cation $NH_4^{\cdot}$, which corresponds to sodion, $Na^{\cdot}$. Since t is combined with only one hydroxyl, it is monovalent, like otassion or sodion. In other respects, also, *e.g.* in the crystalline form of corresponding saline compounds, the ion $NH_4^{\cdot}$, or *ammonion*, is very similar to potassion.

Ammonia must, therefore, be regarded as the anhydride of ammonium hydroxide, NH_4OH. It has not as yet been possible to prepare ammonium hydroxide in the pure state, just as only the anhydride of sulphurous acid, SO_2, and not sulphurous acid itself, H_2SO_3, is known. As to its existence, however, or rather as to the existence of the ion $NH_4^{\cdot}$ or ammonion, no more doubt exists than as to the existence of the ion of sulphurous acid, SO_3''.

This assurance is based chiefly on the fact that there are a large number of salts which can be prepared from ammonia and acids, and which all contain the ion $NH_4^{\cdot}$. To this there belongs a series of definite properties, just as to any other simple or compound ion.

For example, if an aqueous solution of ammonia acts on a solution of hydrochloric acid, the ordinary formation of a salt from acid and base takes place (p. 199), according to the equation

$$NH_4OH + HCl = NH_4Cl + H_2O.$$

Since in the reaction of acids on ammonium hydroxide exactly the same amount of water is formed as was used up in the formation of ammonium hydroxide from ammonia and water, it follows that this water is quite unnecessary for the salt formation, and that the same salt will be obtained by simply bringing ammonia and the acid together. Thus,

$$NH_3 + HCl = NH_4Cl.$$

As a matter of fact, this reaction takes place, and it can be shown very clearly by placing a dish with concentrated hydrochloric acid and one with ammonia side by side in a wide glass cylinder. The two substances come together in the gaseous state, and since the resulting compound, ammonium chloride, NH_4Cl, is not volatile at room temperature, it separates out in the form of dense, white fumes, which form a cloud over the two dishes.

* The formation of fumes occurs in a visible manner with such small quantities of ammonia that it is employed for the detection of that gas. If a glass rod, moistened with hydrochloric acid, is brought to the mouth of a vessel in which ammonia is being developed, the latter is at once detected by means of the formation of fumes.

In the aqueous solution of ammonia, only a small portion of this substance is present as dissociated hydroxide. This is apparent from the fact that the basic properties are not nearly so strongly developed in such a solution as, for example, in a corresponding solution of sodium hydroxide. The electrical conductivity, which is the most convenient measure of the ions present, shows that in a 1 per cent solution of ammonia only about 0·005 of the ammonium hydroxide which could be formed therefrom is dissociated into ammonion and hydroxidion.

It follows, also, from the approximate validity of Henry's absorption law, that the dissolved ammonia is present for the greater part as such (or as a simple hydrate) in solution, and that no great portion is dissociated into ions. In the case of hydrochloric acid, where the opposite is the case, the deviations from the law of Henry are also very great (p. 181). It is apparent, also, from many other phenomena which will be discussed later, that ammonia is a rather feeble base, *i.e.* does not form much hydroxidion.

Ammonia is prepared from the ammonium salts, which are obtained in large quantities as by-products in the manufacture of coal-gas, by warming them with another base. Ammonium hydroxide is first formed; since this, however, is not stable, it decomposes immediately into ammonia and water, the former of which escapes as a gas. Thus, ammonium chloride and caustic soda yield ammonia in accordance with the following equation:—

$$NH_4Cl + NaOH = NaCl + NH_3 + H_2O.$$

For manufacturing purposes, the cheaper calcium hydroxide is employed instead of caustic soda. Since calcium is divalent, the reaction takes place according to the scheme

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O.$$

The ammonia gas is passed into water, and is stored or transported in the form of an aqueous solution. This solution is usually shortly called ammonia, or, also, spirit of hartshorn, a name due to the fact that ammonia was formerly prepared by the distillation of horns, hoofs, etc. The solution smells strongly of the gas which, when the temperature is raised, is given off more or less readily according to the degree of saturation. It forms the most convenient starting substance for obtaining the gas, since it is only necessary to warm it. The water vapour which is carried over with the gas is removed by passing the latter over solid sodium hydroxide.

Since the critical temperature of ammonia gas is 130°, it can be liquefied by pressure at the ordinary temperature. At 10° this can be accomplished by a pressure of 6 to 7 atm.; the boiling point at atmospheric pressure is – 33·5°. At a fairly low temperature the colourless liquid solidifies to a white mass, which melts at – 74°.

On account of the favourable conditions under which it can be iquefied, ammonia is used on the large scale for refrigerating machines or producing low temperatures. The principle of these is that mmonia is liquefied by pressure, the heat which is thereby developed eing led away by means of water at the ordinary temperature. The iquid ammonia is then caused to evaporate, whereby heat is absorbed; he heat is taken from a difficultly freezing salt solution. The latter s thereby reduced to the required low temperature, and is removed to the place where the cold is to be applied. The ammonia which has evaporated again returns to the pump; the salt solution, likewise, is returned to the machine after it has been used for cooling purposes, and its temperature has thereby again risen.

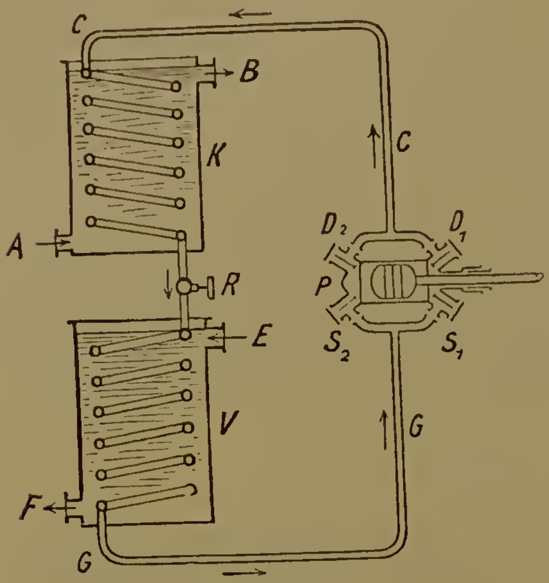


Fig. 93.

A diagrammatic representation of an ammonia refrigerator, such as is almost exclusively used at present, is given in Fig. 93. *P* is the pump, which is fitted with the pressure valves *D* and the exhaust valves *S*. This forces the ammonia to the condenser *K*, where it is liquefied and reduced to the temperature of the condenser water. The liquid ammonia passes through the regulating valve *R* into the evaporating vessel *V*, where it is gasified by means of the pump; the salt solution circulates through the evaporating vessel, passing out at *F*, and entering again in the warmed condition at *E*. In this way a complete cycle is obtained.

Since the heat does not pass of itself from a lower to a higher temperature, work is necessary, and this is performed by the engine which works the pump P. The consumption of work increases with the amount of heat which has to be taken up from the salt solution and with the depression of temperature which it is desired to effect.

In order to show the chemical composition of ammonia, use is made of the decomposition which it undergoes with sodium hypobromite (p. 228). This takes place according to the equation

$$2NH_3 + 3NaOBr = 3NaBr + 3H_2O + N_2,$$

the hydrogen of the ammonia being oxidised by the oxygen of the hypobromite, and the nitrogen set free in the gaseous state. A measured amount of ammonia gas is collected over mercury, and a little water then passed up to it. The rapid ascension of the mercury shows the great velocity with which the gas is absorbed by water. A quantity of hypobromite (obtained by adding 6 cc. of bromine, with cooling, to a solution of 10 gm. of caustic soda in 100 gm. of water) is added to the solution with the aid of a pipette bent at the lower end; nitrogen is evolved which occupies half the volume of the ammonia (after the former pressure has been established), and can be recognised by its property of not burning and of not supporting combustion.

Owing to the fact that it contains hydrogen, ammonia is combustible, but its velocity of combustion is too small for a current of the gas to continue to burn in air. This is possible, however, in pure oxygen. If concentrated ammonia solution is warmed in a small glass until it evolves gas copiously, and oxygen is passed on to the surface of the liquid, the gaseous mixture can be ignited. Around the oxygen tube a greenish flame is formed which burns with a whistling sound. The ammonia does not burn to nitrogen but to nitrous and nitric acids, which combine with the excess of ammonia to form the corresponding salts.

Further, heated platinum catalytically promotes the combustion of ammonia. If a heated spiral of platinum wire is hung in a mixture of oxygen (or air) and ammonia, it continues to glow, and fumes of ammonium nitrate and nitrite are formed.

Of the ammonium salts, that of nitric and of nitrous acid are of especial importance here. The former yields large crystals which very readily dissolve in water, thereby producing a considerable lowering of temperature. If placed on glowing charcoal, it detonates, and when carefully heated decomposes smoothly into water and nitrous oxide—

$$NH_4NO_3 = N_2O + 2H_2O.$$

This is the most convenient and usual method of preparing nitrous oxide (p. 330).

Ammonium nitrite decomposes in a similar way, only much more easily—

$$NH_4NO_2 = N_2 + 2H_2O.$$

That is to say, water and nitrogen are formed. The reaction takes place very readily; it proceeds energetically even below the boiling point of water.

For this purpose it is not necessary to first prepare pure ammonium nitrite, but it is sufficient to bring the ions $NH_4^{\cdot}$ and NO_2' together, *i.e.* it is sufficient, in order to obtain a regular current of nitrogen, to warm a soluble nitrite (*e.g.* commercial sodium nitrite) with an ammonium salt (*e.g.* ammonium sulphate) in aqueous solution.

It has been asserted that the reverse reaction, the combination of free nitrogen with water to form ammonium nitrite, also occurs, especially in the evaporation of water in the air. It must, generally speaking, it is true, be conceded that every chemical process which takes place in a definite direction also takes place in the reverse sense; in all cases it is only a question of *how much* is formed. Although exact determinations have not been made, it may be estimated that the formation of ammonium nitrite from nitrogen and water will most probably ensue only to an exceedingly slight degree, so that it seems very doubtful whether it will be possible to detect the amount formed, or indeed, whether the ammonium nitrite which may be found has been formed in this way.

Amido-compounds.—When potassium is warmed in ammonia gas, it is converted into a white mass, which when fused appears blue; hydrogen is evolved in the process. This mass has the composition KNH_2, and is formed in accordance with the reaction $2K + 2NH_3 = 2KNH_2 + H_2$.

Just as in the case of hydrogen chloride, HCl, and of water, H_2O, one combining weight of hydrogen can be replaced by potassium (or another metal), so, also, it is possible in the case of ammonia, H_3N. This replacement, however, becomes gradually more difficult. Whereas most of the metals can displace hydrogen from hydrochloric acid, only a few can do so in the case of water; and in the case of ammonia, only the alkali metals have this power. The resulting product, also, is rather unstable; on being fairly strongly heated, it decomposes, and in contact with water it is converted into potassium hydroxide and ammonia, in a manner similar to the conversion of a metallic hydroxide into a metallic chloride and water, in contact with hydrochloric acid.

The residue, NH_2, produced by the loss of one combining weight of hydrogen from ammonia, has, in many compounds, a similar significance to the residue of water, hydroxyl. It bears the name *amidogen*, so that the compound KNH_2 is called potassamide, and it is found in many compound substances. Since it is formed from ammonia by the loss of one hydrogen, it is monovalent and can take the place of hydrogen, chlorine, or hydroxyl. The amido-compounds are most readily obtained from (comparatively unstable) chlorine compounds, by acting on these with ammonia. The chlorine is then eliminated along with hydrogen as hydrogen chloride, which mostly combines immediately with more ammonia to form ammonium chloride, and the amide residue takes the place of chlorine—

$$R.Cl + 2NH_3 = R.NH_2 + NH_4Cl.$$

Another method of obtaining amido-compounds consists in the action of ammonia on hydroxyl compounds: $R.OH + NH_3 = R.NH_2 + H_2O$. As a rule, the action takes place only at comparatively high temperatures.

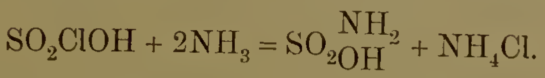
Thus, for example, *sulphurylamide*, generally called shortly *sulphamide*, is obtained by the action of ammonia on sulphuryl chloride: $SO_2Cl_2 + 4NH_3 = SO_2(NH_2)_2 + 2NH_4Cl$. To ensure that the temperature does not rise too high, the sulphuryl chloride is dissolved in a suitable solvent, and the ammonia is passed slowly in.

Sulphamide is a colourless, crystalline compound, which readily dissolves in water, and no longer exhibits the acid properties of sulphuric acid. Also, the solution does not appreciably conduct the electric current, since the substance is not a salt.

On keeping the aqueous solution, the conductivity slowly increases, which shows that a salt is formed. This occurs by the taking up of water: $SO_2(NH_2)_2 + 2H_2O = (NH_4)_2SO_4$. That is, ammonium sulphate is formed.

This reaction is a general one. By the action of water, the amido-compounds pass into hydroxyl compounds plus ammonia. This is the reversal of the method of preparation of the amido-compounds given above; the reversal takes place on the basis of the law of mass action. If the water is removed, the amide can be formed from the hydroxyl compound and ammonia; if, conversely, excess of water is present, it converts the amido compound into the hydroxyl compound.

The question may be asked if an intermediate stage does not exist between the sulphamide and the ammonium sulphate, just as chlorosulphonic acid is an intermediate stage between sulphuryl chloride and sulphuric acid. As a matter of fact, such a compound exists. From chlorosulphonic acid and ammonia, there is formed *sulphaminic acid*—



$$SO_2ClOH + 2NH_3 = SO_2\genfrac{}{}{0pt}{}{NH_2}{OH} + NH_4Cl.$$

In harmony with the fact that acid hydrogen is still present, sulphaminic acid or amidosulphuric acid is a monovalent acid. It is a colourless substance which crystallises well and readily dissolves in water with an acid reaction; the solution is, however, a weaker acid than sulphuric acid. This is a general phenomenon; the entrance of an amido-group reduces the acid properties.

Sulphaminic acid is produced in the form of its ammonium salt by the gradual action of water on the dissolved sulphamide—

$$SO_2(NH_2)_2 + H_2O = NH_4SO_3 \cdot NH_2.$$

By this reaction, sulphaminic acid shows itself still more clearly as an intermediate compound between sulphamide and sulphuric acid.

Sulphaminic acid is also produced by a number of other reactions, some of which will be discussed later.

Sulphaminic acid can also be regarded as a derivative of *ammonia*, which has been formed by one hydrogen of the latter being eliminated as water with one hydroxyl of the sulphuric acid, the two residues NH_2 and HSO_3 then uniting together. The question may be asked if the same reaction may not occur more than once with ammonia, so that two or three of its hydrogens experience the same substitution. Such is the case, the following substances being known:—

Ammonia, $N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.$ Sulphaminic acid, $N\left\{\begin{matrix}H\\H\\SO_2OH\end{matrix}\right.$

Disulphaminic acid, $N\left\{\begin{matrix}H\\SO_2OH\\SO_2OH\end{matrix}\right.$ Trisulphaminic acid, $N\left\{\begin{matrix}SO_2OH\\SO_2OH\\SO_2OH\end{matrix}\right.$

Into the preparation and properties of these substances we shall not enter here; rather, they have been mentioned only for the purpose of showing how conclusions by analogy may furnish a clue in searching for new substances, the possibility of *one* definite reaction giving rise to the presumption that similar reactions are possible. Such conclusions do not always lead to a positive result, since circumstances may exist which show that the analogy in question does not hold, or that it is impracticable. Still the method has proved useful in so many cases that it constitutes one of the most important aids to the progress of science towards the knowledge of new compounds.

The substances we have mentioned do not complete the list of the nitrogen derivatives of sulphuric acid, but we must here forego the discussion of further details.

* In the same way as sulphuric acid, many other hydroxyl compounds can also yield amides and similar derivatives. Thus, for example, there is an amide of nitric acid, NO_2NH_2, obtained by a method which cannot here be discussed; it forms a white, crystalline mass, which at 70° rapidly decomposes into water and nitrous oxide. On account of this decomposability, it cannot be obtained by heating ammonium nitrate, whereas, otherwise, heating the ammonium salts constitutes a fairly general method for obtaining the acid amides.

* **Other Oxygen-Hydrogen Compounds of Nitrogen.**—Besides the compounds of nitrogen already described, there are a number of others which contain both hydrogen and oxygen. The following list gives a review of the entire series of these compounds.

The highest stage of oxidation of nitrogen, viz., nitric acid, can be formally regarded, by the addition of $2H_2O$, as a compound of nitrogen with five hydroxyl groups: $HNO_3 + 2H_2O = N(OH)_5$. Doubling this formula in order to obtain an expression for the nitrogen compounds with 2N, the following series is obtained by the gradual replacement of the hydroxyl groups by hydrogen:—

$N_2(OH)_{10} = 4H_2O + 2HNO_3$: Nitric acid.
$= 5H_2O + N_2O_5$: Nitrogen pentoxide.
$N_2(OH)_9H = 5H_2O + N_2O_4$: Nitrogen peroxide.
$N_2(OH)_8H_2 = 4H_2O + 2HNO_2$: Nitrous acid.
$N_2(OH)_7H_3 = 5H_2O + 2NO$: Nitric oxide.
$N_2(OH)_6H_4 = 4H_2O + H_2N_2O_2$: Hyponitrous acid.
$= 5H_2O + N_2O$: Nitrous oxide.
$N_2(OH)_5H_5 = 5H_2O + N_2$: Nitrogen.
$N_2(OH)_4H_6 = 2H_2O + 2NH_2(OH)$: Hydroxylamine.
$N_2(OH)_3H_7 = 2H_2O + N_2H_5(OH)$: Diamide hydrate.
$= 3H_2O + N_2H_4$: Diamide.
$N_2(OH)_2H_8 = 2NH_4(OH)$: Ammonium hydroxide.
$= 2H_2O + 2NH_3$: Ammonia.
$N_2(OH)H_9$: Unknown.
$N_2H_{10} = 2NH_5$: Unknown.

According to this table, ammonia appears as the last known member of the series of reduction compounds of nitric acid, and between it and nitrogen, which stands in the middle, two stages are present which are known, and to which the names hydroxylamine and diamide (or hydrazine) have been given.

Hydroxylamine, NH_3O, is formed under various conditions by the reduction of nitric acid or other oxygen compounds of nitrogen. It is obtained chiefly in the form of a hydrochloride, from which the pure compound can be obtained by decomposition with a base, with exclusion of water, and distillation under reduced pressure. Hydroxylamine is a crystalline substance which melts as low as 33° and very readily decomposes. At a high temperature, it decomposes with explosion; on a moderate rise of temperature, it decomposes with violent evolution of gas.

Hydroxylamine dissolves in water, yielding a liquid with an alkaline reaction. The aqueous solution is obtained more readily by decomposing the salts of hydroxylamine with suitable bases, *e.g.* the sulphate with barium hydroxide (p. 290). On distilling the aqueous solution, part of the hydroxylamine passes over with the vapour.

As must be concluded from the alkaline reaction, there exists in the solution a base which splits off hydroxidion. Since all the salts of hydroxylamine are constituted according to the formula $NOH_4 . A$, where A signifies a monovalent anion, the constitution of the basic substance in the aqueous solution is $NOH_4 . OH$, since $NOH_4^{\cdot}$ is the cation of the hydroxylamine salts.

This is an exceedingly feeble base, and is much less dissociated than ammonia. On account of its decomposability, its electrical conductivity has not yet been determined with accuracy.

Hydroxylamine is very unstable to oxidising agents both in the free state as well as in its salts, and passes readily into nitrogen and water: $2NOH_3 + O = N_2 + 3H_2O$.

The oxygen contained in hydroxylamine and in its salts, has been regarded as united with hydrogen to form hydroxyl, and the substance has, therefore, received the formula $NH_2(OH)$, in accordance with which assumption the name also has been formed. The base present in aqueous solution would, therefore, have the formula $NH_3(OH)_2$, and as, according to this, it contains two hydroxyls, it would be divalent and could form salts of the type $NH_3 . A_2$, where A is a monovalent anion. Such salts are not known, and there is, therefore, in this direction, no immediate foundation for the above assumption. The fact, however, that hydroxylamine is such a feeble base makes the possibility of the formation of di-acid salts recede greatly into the background. For the oxyacids, indeed, are hydroxyl compounds in which no basic properties can be recognised. The non-existence of divalent salts is, therefore, no proof against the assumption that the oxygen in hydroxylamine forms a hydroxyl group, and since other facts (belonging to organic chemistry) speak in its favour, that formula may be retained.

Hydrazine.—A further reduction product of nitrogen, of basic character, the basic properties of which are intermediate between those of hydroxylamine and ammonia, can likewise be obtained by the reduction of the higher oxygen compounds under certain conditions, which cannot be described here. This compound has the composition N_2H_4, and can be obtained from the corresponding salts by decomposition with bases, with elimination of water.

The substance has received the name hydrazine (from azote = nitrogen); it is also called diamide, since the atomic group NH_2 has long been called amide.

Hydrazine is a colourless liquid which boils at 114° and solidifies at 1°. It combines with water to form a hydrate N_2H_6O, which is volatile without decomposition. In a further quantity of water it dissolves, yielding a liquid with an alkaline reaction, from which the salts of hydrazine can be obtained by neutralisation with acids.

Two series of such salts are known, monacid and diacid. The former have the composition $N_2H_5 . A$, the latter, $N_2H_6 . A_2$. The corresponding hydroxides are, therefore, $N_2H_5(OH)$ and $N_2H_6(OH)_2$.

The salts of the second series are, however, very unstable and readily decompose into salts of the first series and free acid. In aqueous solution, the same decomposition takes place almost completely. The aqueous solution, therefore, even of the free base consists essentially of $N_2H_5(OH)$ and of the ions of this monacid base, viz., $N_2H_5^{\cdot}$ and OH'. The ions formed from this by accession of water, $N_2H_6^{\cdot\cdot}$ and $2OH'$, are present to quite a small extent.

The solutions of hydrazine have a powerfully reducing action, and exceed in this respect even the hydroxylamine solutions.

Hydrazoic Acid.—The last compound of this series which we shall mention here is hydrazoic acid, HN_3. It did not find a place in the general summary given on p. 344, since it contains three combining weights of nitrogen, and that list was extended only to two combining weights of that element.

Hydrazoic acid was first obtained by the decomposition of organic compounds of complex composition; not until later was a method discovered for preparing it from simpler substances. One of the simplest methods of preparation is from hydrazine and nitrous acid in aqueous solution. There occurs the reaction $N_2H_4 + HNO_2 = HN_3 + 2H_2O$. Further, the sodium salt of hydrazoic acid, NaN_3, is obtained by passing nitrous oxide over heated sodamide (p. 342). The reaction is $NH_2Na + N_2O = NaN_3 + H_2O$. The acid can be obtained from the sodium salt by distillation of the aqueous solution after the addition of sulphuric acid.

On distilling the aqueous solution obtained by one or other method, the acid first passes over and can in this way, finally also by the use of dehydrating agents, be obtained in the pure state. Hydrazoic acid is thus obtained as a colourless liquid with a strong and very unpleasant smell, which boils at 37°, and explodes very readily with great violence. The same property is also possessed by many of its salts in the solid state. In solution, however, the acid is fairly stable.

In the case of this compound, the acid properties are clearly although not very strongly developed: a 1 per cent aqueous solution is dissociated to the extent 0·008 into its ions. On account of the slight dissociation, it can be separated from its aqueous solutions by distillation. The ions of the acid are hydrion, and the group N_3'; the salts of the acid are, therefore, sometimes called metallic nitrides.

Organic Nitrogen.—It has already been mentioned that nitrogen is an essential component of all living organisms, and is found especially in those substances whose changes appear closely bound up with vital activity. It is, therefore, of great importance to understand the circulation of this element in the organised world.

Since free nitrogen is indifferent and no substance is known which interacts with it at ordinary temperature, it was long believed that all organisms must carry on life with that amount of combined nitrogen which is at their disposal on the earth's surface. In fact, the action of manure from animal excrement depends in large degree on the fact that it contains combined nitrogen, which is taken up by the plants and subsequently passes again into the animal organism.

Besides this nitrogen, rain water always contains small quantities of ammonia, which may partly be formed from animal nitrogen which has been evolved in the form of ammonia and is taken up from the air by rain. The ammonia of rain water, however, frequently occurs in the form of ammonium *nitrate*, and the nitric acid which is required for this probably owes its existence to electric discharges in the air, whereby free nitrogen is made to combine with oxygen. Here we have at least one source of combined nitrogen by which our capital in that can be increased.

Further, it has recently been found that certain low forms of life form substances which can unite with free nitrogen and convert this into the combined state. These organisms occur partly alone, but chiefly in vital association (symbiosis) with higher plants, especially the papillionaceæ or leguminosæ (lupines, clover, beans, peas), in whose roots they reside. The amount of combined nitrogen is likewise increased by these plants. There appears, therefore, to be no immediate danger of the earth becoming impoverished with respect to its combined nitrogen.

CHAPTER XV

PHOSPHORUS

General.—The name phosphorus (light-bearer) was formerly used t designate all substances which possess the property of emitting ligh without at the same time having a correspondingly high temperature The name phosphorescence, used in physics for the after luminescenc shown by certain substances after a previous exposure to light, is a relic of that usage. At the present day, the name phosphorus is confined to one element, which also exhibits the above property of col luminescence, although for a different reason.

Phosphorus was discovered about the year 1670 by an alchemis Brandt, who obtained it by the distillation of the residue left on the evaporation of human urine. He kept his method secret, but it was soon found out by Kunkel in Germany, and Boyle in England. Gahn and Scheele also soon found that the bones of the vertebrate animals were a much richer source of phosphorus, and at the present day it is still chiefly prepared from these.

The method of obtaining phosphorus depends on the fact that the oxygen compound of phosphorus, phosphoric acid, which is containe in the bones, is reduced by charcoal. The charcoal combines with the oxygen, and the phosphorus is set free and distils over. The reaction cannot be given here in detail, but will be more fully described later (Chap. XXIII.).

In nature, phosphorus occurs only in the form of salts of the just mentioned phosphoric acid. These compounds are very wide-spread, although they do not occur anywhere in large quantities. They are o great importance for organic life, since the "protoplasm" of the cells the substance to which the actual vital activity is attached, always contains small amounts of phosphorus compounds. The nerve and brain substances, more especially, are comparatively rich in phosphorus which is there present in the form of phosphoric acid derivatives.

Phosphoric acid is also indispensable for the growth of plants. As the soil does not usually contain much of it, this substance is, for the purpose of high cultivation, added to the soil. The artificia manures containing phosphoric acid play a very important rôle in agriculture.

The Allotropic Modifications of Phosphorus.—Elementary phosphorus occurs in two very different forms, with properties so unlike that they would, at first sight, be taken for quite different substances. The variety of phosphorus which has been longest known is formed when the vapour of the substance is quickly cooled, which occurs, indeed, in the preparation. The vapour then condenses to a wax-like mass which, in the pure state, is almost colourless; it melts at 44°, boils at 287°, is readily soluble in various solvents, and is luminous in the air, at the same time emitting fumes. This *white phosphorus* can be readily obtained in fine crystals belonging to the regular system and having a diamond lustre, by allowing solutions of phosphorus (*e.g.* in carbon disulphide) to slowly evaporate, with exclusion of air. Crystals are also obtained when the slow sublimation of the phosphorus is effected by a slight difference of temperature in a vacuum.

The smoking and luminescence of white phosphorus in the air, depends on the fact that it combines with the oxygen of the latter and passes into various oxidation products, which shall be described later. Phosphorus, on lying exposed to the air, therefore, diminishes in amount, and finally liquefies to an acid liquid, which is the solution of the above products of oxidation in the water abstracted from the air.

White phosphorus, on being even gently warmed in the air, takes fire and burns with a brightly luminous flame. The appearances seen here have already been described (p. 16).

The second form, *red phosphorus*, behaves quite differently from the white variety. It is obtained by heating white phosphorus out of contact with the air, to a temperature of 250° to 300°. Red crusts then separate from the colourless, liquid phosphorus, and almost the entire amount is gradually converted into a red, solid mass. If this is freed by suitable solvents from the ordinary white phosphorus which s still present in small quantities, a dark red powder is obtained, which remains for a long time unchanged in the air, does not appreciably dissolve in the solvents for white phosphorus, does not become uminous, and can be heated to a fairly high temperature without becoming ignited. Further, red phosphorus is not poisonous, whereas white phosphorus is highly so.

That these two substances, so different in appearance, are both elementary phosphorus, is seen, on the one hand, from the fact that the one can be converted without residue into the other, and, on the other hand, from the fact that both, when subjected to the same actions, yield the same transformation products in equal amounts.

Red phosphorus is frequently called amorphous phosphorus. This designation is incorrect; the small scales of which red phosphorus consists are found, on microscopic examination, especially in polarised light, to be crystalline. The conversion of white phosphorus into re is accompanied by an evolution of heat equal to 114 *kj*.

Reciprocal Transformation of the two Kinds of Phosphorus.—That red phosphorus is formed from white by heating has already been mentioned. The velocity of this change depends very greatly on the temperature; at 300° it is moderate, at 350° however, it is very great, so great, indeed, that explosion readily takes place. For, since a considerable amount of heat is set free in the transformation, the temperature of the phosphorus rises spontaneously, and the velocity of transformation becomes thereby so increased that a portion of the phosphorus can be vaporised by the heat produced.

The velocity of transformation can be very greatly increased by means of catalytically acting substances, so that the amount of transformation even at a low temperature is considerable. Such a catalytically accelerating agent has been found in iodine, which is effective even when present in very small amount.

Light exercises a similar, accelerating influence. Sticks of white phosphorus which have been kept for some considerable time in a glass bottle, become covered with a red layer which consists essentially of red phosphorus. In such a case, it can generally be clearly seen that the outside parts, which have been most strongly exposed to the light, are correspondingly darker in colour.

Although such different conditions are known under which white phosphorus passes into red, there is only one method for effecting the reverse transformation. It consists in converting the red phosphorus into vapour and quickly cooling this. The vapour always condenses then to colourless liquid or solid phosphorus.

If these facts are examined in the light of the relationships which we have seen to exist between polymorphous substances, *e.g.* in the case of sulphur (p. 254), we must regard the white phosphorus as the unstable form compared with the red. This view is supported by the various spontaneous transformations which take place at comparatively high temperatures, and under the influence of catalysers and of light, although the latter circumstance is not without doubt. The much greater solubility of white phosphorus also supports the above view.

The formation of white phosphorus from the vapour, is another case of the law that the less stable form first appears (p. 207).

In the case of polymorphous substances, now, there are two possibilities. Either the two forms can have a transition point on either side of which the relative stability changes, as is the case with sulphur (p. 254); or, as in the case of iodine monochloride (p. 238), the one can be the stable, the other the unstable form, throughout the whole accessible range of temperature up to the melting point. Substances of the first kind are called enantiotropic, those of the second, monotropic. In the case of white and red phosphorus, is the relationship one of enantiotropy or of monotropy?

At fairly high temperatures, red phosphorus is certainly the more stable, since it is produced spontaneously from the white. At lower temperatures, the relationship is also the same, as is proved by the greater solubility of the white form. Consequently, phosphorus must be regarded as monotropic, and the red phosphorus is under all circumstances the more stable form compared with the white. It is also the more stable form with reference to liquid phosphorus, since, indeed, the conversion into red phosphorus at higher temperatures takes place from the liquid, because white phosphorus melts as low as 44°.

Objection could be taken to this view on the ground that white phosphorus can be kept for a very long time, even in contact with the red form, without transformation taking place. This, however, only proves that the velocity of transformation at room temperature is very small. This is not a mere assumption made to explain the present relations, but is seen to be in accordance with the rule when the following facts are kept in view.

As has already been mentioned several times, the velocity of chemical reaction increases with a rise of temperature in such a way that a rise of 10° or 15° corresponds to a doubling of the velocity, and the reverse holds for a lowering of temperature. Now, the transformation at 250° takes place in a few hours; assume it to occur in one hour, and assume, further, that a doubling of the velocity takes place only with every 15°, then the reaction at 10° lasts 2^{16} hours, or about eight years. If we assume, however, that the velocity is doubled by a rise of 10°, then the time of transformation at 20° is found to be 1000 years. This rough calculation shows that the assumption of a very small velocity of transformation at room temperature contains nothing contradictory to fact.

The Oxidation of Phosphorus in Air.—Not only does there attach to the slow combustion of phosphorus in the air the historical interest that it led, by reason of the peculiar emission of light, to the discovery of this element, but there still exist at the present day questions of scientific interest with relation to this long-known phenomenon, which have not as yet received a satisfactory answer.

Phosphorus is luminous in the air at ordinary temperatures, and at he same time undergoes oxidation. The higher the temperature rises, the more vigorous does this slow combustion become, passing, at about 45°, into rapid combustion.

If the concentration of the oxygen is diminished, *e.g.* by allowing the phosphorus to undergo oxidation in a confined space, the luminescence continues till the last detectable trace of oxygen is used up. Even exceedingly small amounts of oxygen are sufficient to bring about the luminescence, and it was a matter of difficulty to show that oxygen was, indeed, present in all cases in which luminescence occurred.

* On the other hand, even very small quantities of phosphorus are sufficient to give rise to the luminescence in the air. This phenomenon is, therefore, employed for the detection of traces of phosphorus, *e.g.* in cases of poisoning. For this purpose, the mass to be investigated is placed along with water in the flask *K* (Fig. 94), and heated to boiling. The vapours are conducted through a twice-bent tube into the condenser *R*. If phosphorus is present, a luminous ring appears in the dark at the point *a*, where the aqueous vapour and, along with it, the phosphorus vapour are condensed.

It might be expected that the luminescence in pure oxygen would be especially vigorous. This, however, is not the case; phosphorus does not become luminous at all in pure oxygen under atmospheric pressure. On diminishing this, the luminescence commences at a definite pressure, which depends on the temperature, and which is all the greater the higher the temperature. The fact, therefore, that phosphorus is luminous in ordinary air is due to the partial pressure of the oxygen of the air being below this special pressure: the temperature of − 7°, at which the "luminescence pressure" in pure oxygen is $\frac{1}{5}$th atmosphere, is also the limit for luminescence in air.

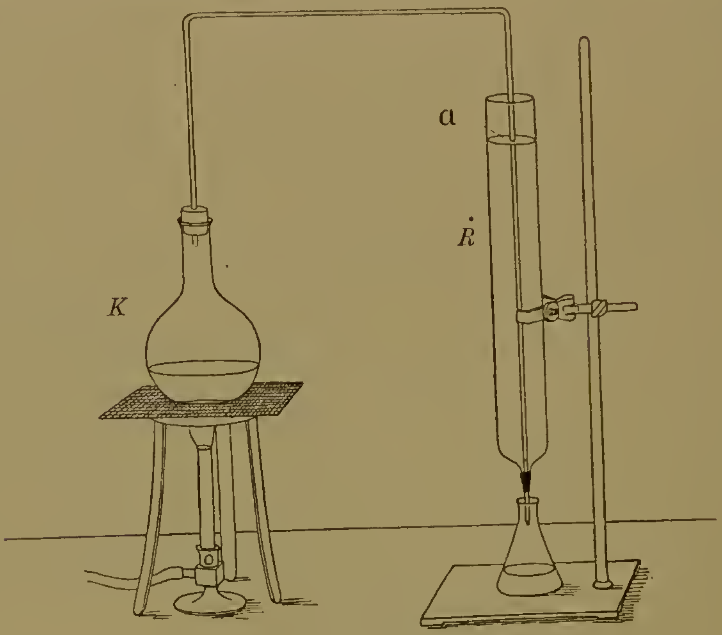


Fig. 94.

The nitrogen acts as a diluent, and exerts no specific influence on the phenomenon. Many other gases, especially the vapours of organic substances, such as oil of turpentine or alcohol, behave differently: they prevent the luminescence, even when they are present in very small amount. The reason is a great retardation of the velocity of reaction between phosphorus and oxygen; the phenomenon is, therefore, a catalytic one. This behaviour is of importance for the abovementioned method of detecting phosphorus by means of the luminescence, since it can make it appear as if phosphorus were absent when, in reality, it is present.

Ozone (p. 79) is formed in the slow combustion of phosphorus in the air, and can be readily recognised by its smell; that which is usually termed phosphorus smell is nothing but the smell of ozone. The vapour of phosphorus itself has a smell like garlic. One can convince oneself of this by preventing the destruction of the vapour by adding traces of a substance which prevents the slow oxidation. If a clean stick of phosphorus, half covered with water, is allowed to oxidise in a large flask, whereby it is advantageous to slightly raise the temperature, the air of the flask soon becomes full of ozone, and the reactions of this substance given on p. 79, especially the turning brown of potassium iodide and the bleaching of litmus, can be easily demonstrated.

Since ozone is a substance which is formed from oxygen by the absorption of free energy, this energy must come from somewhere else. Evidently, it is the oxidation of the phosphorus which yields this energy. In accordance with the principle stated on p. 203, such a process can be brought about only by a *coupled* reaction, and it must, therefore, be concluded that the formation of ozone takes place in such a way that the ratio of the amount of oxidised phosphorus to that of the ozone produced is definite and a whole number. This is, indeed, the case; the experiments made on this point have shown that equal amounts of oxygen are used up for the oxidation of phosphorus and for the formation of ozone. It has, however, not yet been established what the chemical reaction here is.

Phosphorus Vapour.—The combining weight of phosphorus is found, from its chemical relations, to be 31; the molar weight of phosphorus, calculated from its vapour density, has been found, however, equal to 124, so that to this vapour the formula P_4 must be ascribed. In this respect, therefore, phosphorus differs essentially from nitrogen, to which it exhibits many points of resemblance in the case of its compounds, and is related to sulphur.

At very high temperatures, the density of phosphorus vapour becomes less. Exact measurements of the progress of this process, which presumably consists in the transformation into P_2, are not known.

In accordance with the relations existing between white and red phosphorus, as described on p. 350, the two forms have a very different vapour pressure, the white having a much higher one than the red. Since the transformation of the one form into the other occurs comparatively slowly, both equilibria, that between white phosphorus and its vapour and that between red phosphorus and its vapour, can be observed. These relations are represented in Fig. 95. Above 400° white (liquid) phosphorus cannot be investigated, as its conversion into the red form is too rapid.

* As can be seen from Fig. 95, the vapour pressure of red phosphorus is at 350° still much smaller than that of the white at 200°. It must, therefore, be possible to distil phosphorus from a colder spot to a warmer, if we have white phosphorus at the former and red at the latter. This apparent impossibility has been confirmed by experiment. This reversal of the usual state of affairs on distillation, is due to the fact that the distillate consists of something else than the distilling liquid. Distillation can take place only with diminution of the free energy, whereas, in the case of any definite substance, the free energy certainly increases with rise of temperature. In this case, however, the loss of free energy in the conversion into the red form is so great that it more than counterbalances the increase due to a moderate rise of temperature.

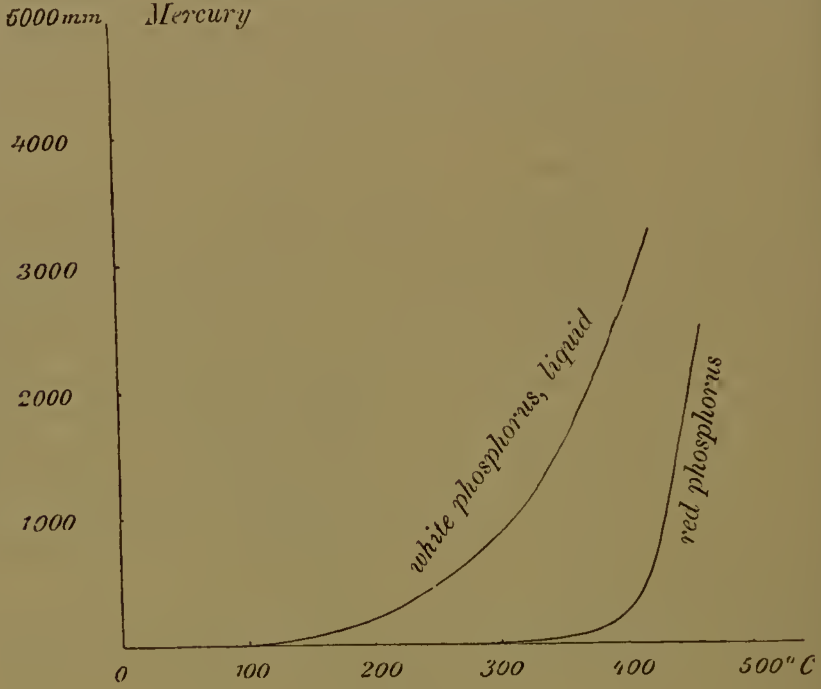


FIG. 95.

Application of Phosphorus.—The low temperature at which phosphorus takes fire, has given rise to its technical application in the preparation of matches. The ends of small strips of wood which have been rendered readily inflammable by coating with sulphur, soaking with paraffin, or by slightly charring, are covered with a mass consisting of phosphorus and a substance rich in oxygen (pyrolusite, potassium chlorate, or such like) along with a cement (gum or dextrine). The cement encloses the phosphorus and protects it from oxidation by the oxygen of the air; the oxygen compound added accelerates the combustion. Owing to the rise of temperature produced on rubbing this mass on a rough surface, the temperature of ignition of the phosphorus is exceeded at some point, the mass takes fire, and the combustion is communicated to the wood by means of the intermediate substance.

On account of the poisonousness of white phosphorus, which can give rise to serious illness in the workers, endeavours have been made to avoid its use. The heads of the so-called Swedish safety matches do not contain any phosphorus, but only mixtures of combustible substances and substances containing oxygen, the temperature of ignition of which is so high that it cannot be reached by rubbing, or can be so only with difficulty. Ignition is effected by using a rubbing surface composed of red phosphorus along with some additions; on rubbing, some of this combustible mass is brought into contact with the material of the match-head, and the temperature necessary for ignition is produced.

Hydrogen Compounds of Phosphorus.—When white phosphorus is heated with caustic soda solution, a gas is evolved which has the remarkable property of igniting spontaneously in the air. This gas consists of phosphorus and hydrogen; in conformity with its density, 34, and the fact that it is composed of one combining weight of phosphorus to three of hydrogen, it must receive the formula PH_3. The reaction which occurs here will be explained presently.

If the gas is collected without access of air, it is found to be colourless, and only slightly soluble in water, and to have a powerful smell like putrefying fish. It readily undergoes decomposition. Even on being gently heated, as well as under the action of light, it decomposes into hydrogen and phosphorus, which separates out in the red form when the decomposition takes place in light. The gas can also be readily decomposed by the electric spark.

* Hydrogen phosphide can be mixed with pure oxygen without igniting spontaneously. If, however, the pressure under which the mixture stands is diminished, explosion and combustion of the hydrogen phosphide suddenly occurs at a definite small pressure, which depends on the proportions of the two gases and on the temperature. This phenomenon exactly recalls the behaviour of phosphorus itself, which can also combine with oxygen only when the pressure of the latter does not exceed a definite value. It is very possible that we are dealing in both cases with the same phenomenon, since the hydrogen phosphide, in consequence of its ready decomposability, will always contain traces of phosphorus vapour.

If the spontaneously inflammable gas is kept some time, it loses the property of spontaneous inflammability, although analysis cannot detect any essential difference. It was, therefore, at first thought that two different kinds of hydrogen phosphide of the same composition existed, until it was found that the property of spontaneous inflammability belonged not to the pure hydrogen phosphide PH_3, but to another hydride of phosphorus having the composition P_2H_4, which is produced in small amount along with PH_3, and whose presence is the cause of the spontaneous inflammability.

This can be proved by passing the spontaneously inflammable hydrogen phosphide through a freezing mixture. The less volatile, spontaneously inflammable hydrogen phosphide separates out, and the issuing gas has now lost the property of igniting spontaneously.

The composition of hydrogen phosphide recalls that of ammonia, and in view of the manifold resemblance between nitrogen and phosphorus, basic properties will also be looked for in the case of hydrogen phosphide. As a matter of fact, these exist, but in exceedingly slight degree.

Hydrogen phosphide combines most readily with the halogen hydracids, above all with hydriodic acid. Both gases combine directly on being brought together, forming a crystalline mass which has the same crystalline form as ammonium chloride. Its composition is represented by the formula PH_4I, exactly corresponding to ammonium chloride, NH_4Cl. On attempting, however, to dissolve this white mass, which bears the name phosphonium iodide (phosphonium = PH_4), in water, hydrogen phosphide is evolved, and we are left with only a solution of hydriodic acid.

* In order to obtain phosphonium iodide, it is not necessary to prepare the two gases separately, but it can be obtained in one operation by the action of phosphorus and water on iodine. For this purpose, white phosphorus (4 parts) is placed in a retort along with iodine (10 parts), and carefully heated with water (3 parts). A twofold reaction takes place, one portion of the phosphorus withdrawing oxygen from the water, so that the hydrogen can combine with the iodine to hydrogen iodide. On the other hand, the hydrogen so produced goes to form hydrogen phosphide. The total reaction can be expressed by the equation $5I + 9P + 12H_2O = 4HPO_3 + 5PH_4I$.

The above mentioned hydrogen phosphide, which inflames spontaneously in the air, has the composition P_2H_4; it is a colourless liquid, which boils at 57°. It is an unstable substance, and in light as well as in contact with various catalytic substances it yields a yellow, solid substance, P_4H_2, or solid hydrogen phosphide, hydrogen phosphide gas being formed at the same time.

Halogen Compounds of Phosphorus.—Phosphorus combines in several proportions with all the halogens, so that we have here a large variety of different compounds. These are mostly very reactive, *i.e.* have a tendency to undergo decompositions with other substances, and are used as important reagents in many preparations.

If chlorine is passed over phosphorus contained in a retort from which the air has been previously displaced by carbon dioxide, in order to prevent the phosphorus igniting spontaneously, direct combination of the two takes place. The heat thereby developed is sufficient to vaporise the greater part of the compound formed, and this condenses, therefore, in the receiver as a colourless liquid.

The reaction proceeds in the above manner when a sufficient amount of phosphorus is present; if, however, the chlorine is in excess, another substance is formed, which will be discussed later.

The above substance is obtained in the pure state by distillation, some phosphorus being added to retain any excess of chlorine which may be present. It forms a colourless liquid which boils at 76°, and has a density 1·6. The molar weight of the vapour is 138. According to this, and in accordance with the results of analysis, it has the formula PCl_3; it is called *phosphorus trichloride*, or, in view of the existence of a higher chloride of phosphorus, *phosphorous chloride.*

Phosphorus trichloride reacts readily with water and other substances containing hydrogen and oxygen. The reaction thereby proceeds in such a way that the chlorine combines partially or entirely with hydrogen to form hydrogen chloride, while the oxygen unites with the phosphorus to form an acid, phosphorous acid, which will be described later. In this way phosphorus trichloride acts as a dehydrating agent, and it is not necessary that the water should be present as such, but may be represented in the compounds merely by its elements. The reaction has nothing to do with the "predisposing affinity" (p. 361), for as the hydrogen and the oxygen here experience quite different fates, they need not have previously stood in any direct relation to one another.

The above mentioned decomposition is also brought about by the water vapour of the air, and for this reason phosphorus trichloride fumes when its vapour comes in contact with moist air.

In the formation of the trichloride, 316 *kj* are developed.

When chlorine is allowed to act on phosphorus or on the trichloride it is readily absorbed, and there is formed a solid substance of a pale yellowish-green colour, which contains five combining weights of chlorine to one combining weight of phosphorus, and is therefore called *phosphorus pentachloride* or *phosphoric chloride.*

Phosphorus pentachloride, PCl_5, does not melt under the ordinary pressure, since its boiling point lies below its melting point. Since, however, the boiling point of all substances rapidly rises as the pressure increases, whereas the melting point is affected to scarcely an appreciable extent by pressure (p. 129), the boiling point can, by increasing the pressure, be brought nearer and nearer to the melting point and finally reach it. In the case of phosphorus pentachloride this temperature is 148°, and the pressure amounts to several atmospheres. Under these circumstances, the pentachloride can simultaneously exist in the solid, liquid, and vaporous states, just as, *e.g.*, water can at 0°

(more exactly, at + 0·0073°; p. 131). Under a still greater pressure, the pentachloride behaves like most other substances; it first melts, and afterwards boils if the temperature is further raised.

In accordance with the formula PCl_5, the vapour of phosphorus pentachloride should have the molar weight 208. The determination of this, however, shows that this value is never reached, but that the actual density of the vapour is less. The difference varies, being greater the higher the temperature and the lower the pressure. In this respect, the vapour of the pentachloride behaves in a perfectly similar manner to the vapour of nitrogen peroxide (p. 324).

Here also, it can be assumed that the vapour is not a single substance, but that the pentachloride in the vaporous state partially dissociates into phosphorus trichloride and chlorine, in accordance with the equation $PCl_5 = PCl_3 + Cl_2$. Such a mixture of trichloride and chlorine must have half the density of the vapour of the pentachloride, for, as the equation shows, one volume of the vapour is converted into two volumes of its decomposition products. The observed values of the molar weight lie between the two limits 208 and 104, and from the densities observed under given conditions the proportions of trichloride vapour and chlorine which would yield a mixture of that density can be calculated (p. 325).

* Confirmation of this view can be obtained in the following manner. The vapour of the pentachloride has the yellowish-green colour of chlorine only in a slight degree. If, now, it be ascertained in what proportions chlorine must be mixed with any colourless gas in order to yield a gas of the same colour as the pentachloride vapour, it may be concluded that the same proportion of chlorine is contained in both. The determination made in this way of the amount of chlorine in the vapour of the pentachloride agreed sufficiently with the value calculated from determinations of the density, on the assumption of a partial dissociation into trichloride and chlorine.

Phosphorus pentachloride fumes strongly in the air and has a powerful irritant action on the mucous membranes, so that care must be exercised in working with it. With water it rapidly undergoes decomposition, with formation of phosphoric and hydrochloric acids (*vide infra*). The pentachloride, also, acts on many other compounds similarly to the trichloride. In this case, however, it is chiefly the large amount of chlorine contained in the compound which in the first place comes into action, and the pentachloride is, therefore, an agent for introducing chlorine into other compounds. More especially does it act on hydroxyl compounds in such a way that chlorine takes the place of the hydroxyl; the pentachloride thereby passes into phosphorus oxychloride, a compound which will be described later. In consequence of this reaction it is widely applied, especially in organic chemistry.

The heat of formation of phosphorus pentachloride is 440 *kj*: in the conversion of the trichloride into the pentachloride by free chlorine, therefore, a considerable quantity of heat, viz., 124 *kj*, is developed.

The Other Halogen Compounds of Phosphorus.—Phosphorus unites with bromine to form two compounds which are quite similar to those of chlorine and exhibit corresponding reactions. Phosphorus tribromide, PBr_3, is a liquid which boils at 175°, and phosphorus pentabromide is a yellow-brown solid whose vapour contains free bromine.

Such a great similarity to the chlorine compounds is, however, not shown by the iodine compounds of phosphorus. Phosphorus triiodide, PI_3, is a red, crystalline substance which is formed from its elements with slight evolution of heat. A phosphorus pentaiodide is not known. There exists, however, a well-characterised subiodide of phosphorus which, in accordance with its composition and vapour density, has the formula P_2I_4, and is also a red, crystalline substance. This iodide can also be obtained by the direct union of the elements, which takes place with slight rise of temperature. It is better to dissolve both in a common solvent, *e.g.* carbon disulphide, whereby combination takes place immediately, and then to distil off the solvent with exclusion of moisture. The compound is thus obtained in pure, fine red crystals.

Both compounds are decomposed by water into oxyacids of phosphorus and hydriodic acid, and serve, therefore, for the preparation of the latter (p. 233). If a small amount of water and a comparatively high temperature are employed, a portion of the phosphorus also combines with the hydrogen of the water, and phosphonium iodide is formed (p. 356).

Only one compound of phosphorus with fluorine is known; this has the formula PF_5. This is a gas which is rapidly decomposed by water, and which at medium temperatures passes into a liquid only under a high pressure.

The heat of formation of phosphorus tribromide is 187 *kj*, that of the pentabromide, 247 *kj*; that of phosphorus diiodide, P_2I_4, is 82 *kj*.

Oxygen Compounds of Phosphorus.—Similarly to most of the elements hitherto discussed, phosphorus forms with oxygen and hydrogen a number of acids which differ from one another by containing different amounts of the former. These compounds, however, differ from the previous ones in the fact that they are in general *polybasic*, *i.e.* contain several combining weights of hydrogen replaceable by metals.

The most important of these compounds is *phosphoric acid*. This name embraces several acids, all of which can be regarded as hydrates of the same anhydride, P_2O_5, phosphorus pentoxide, but which differ from one another in the different proportions of water and anhydride. Such differences have already been met with in the case of sulphuric acid and sulphurous acid; they could, however, be detected only in the case of the salts, and disappeared in the solutions of the free acids. In the case of the phosphoric acids, the differences remain for a measurable period of time even in aqueous solution, and furnish evidence for the propriety of the view expressed in the previous cases.

Phosphorus Pentoxide.—This substance, which is produced in the rapid combustion of phosphorus in the air or oxygen, we have already repeatedly met with. It can be obtained in any desired amount by means of the apparatus shown in Fig. 96. *A* is a cylinder of sheet-iron through which, by means of the side tubes *a* and *b*, a current of air dried with sulphuric acid is passed. Within the cylinder there hangs a dish in which burning phosphorus is placed at the commencement of the experiment. When this has burned away, it is only necessary to throw in small pieces of phosphorus through the short tube *c*: in the warm dish the phosphorus takes fire spontaneously. The phosphorus pentoxide produced forms a loose, snow-like mass which, after opening the lower tube *d*, can be shaken down into a dry vessel.

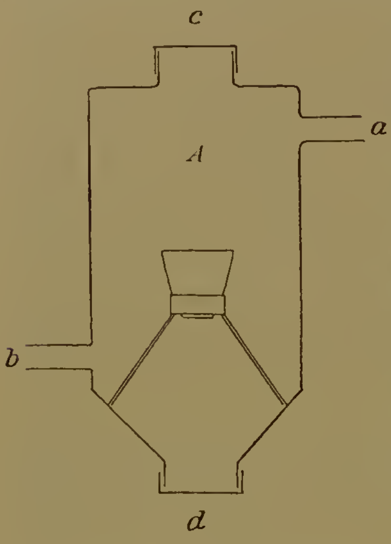


FIG. 96.

Phosphorus pentoxide has the composition represented by the formula P_2O_5, and is the highest known oxide of phosphorus. It is a white mass, which sublimes at a low red heat. When obtained by the combustion of phosphorus, it is not quite pure; apart from traces of water, which it has generally attracted, it usually contains some phosphorus trioxide in consequence of incomplete combustion. It can be purified by sublimation in a current of dry oxygen.

The most striking property of the pentoxide is its great tendency to absorb water. It rapidly becomes liquid in the air; if thrown into water, it combines with the latter with a hissing sound in consequence of the strong development of heat. The pressure of the aqueous vapour from the resulting compound is exceedingly small, so that phosphorus pentoxide is the most effective desiccating agent known. It is used in all cases where it is desired to withdraw the last removable traces of water vapour. If it is to be used for drying gases, it is well to absorb most of the water vapour by means of an ordinary desiccating agent, *e.g.* sulphuric acid, and to use the pentoxide only for the final drying.

Besides being employed for absorbing existing water, phosphorus pentoxide is used to bring about reactions which take place with elimination of water. An example of this has already been cited in discussing nitrogen pentoxide (p. 322). Such reactions were formerly ascribed to a peculiar kind of chemical affinity, the *predisposing affinity.* It was assumed that a substance which has a great affinity to a definite compound can bring about the formation of this compound from its elements. Such a view, however, contains the assumption that the affinity to a substance, which is as yet quite absent, brings about the reaction which leads to its formation, *i.e.* an assumption that an action proceeds from a thing which is not present.

The proper manner of regarding this and similar reactions, is to be sought in the law of mass action. Nitric acid is decomposed in a very slight degree into water and anhydride[1]; if phosphorus pentoxide is added, the water is converted into another compound, and fresh acid must decompose into water and pentoxide, in order that equilibrium may be again established. This process is repeated until one of the participating substances is exhausted, or until a chemical equilibrium is established between the new substances.

* The assumption here made that those substances whose formation from given substances as a result of known reactions is possible, are in reality present, although frequently in immeasurably small amount, is no arbitrary assumption, made to "explain" otherwise unexplained phenomena, but it is demanded by the laws of thermodynamics, which is one of the best founded general postulates. The proof of this, certainly, cannot be given here.

The Phosphoric Acids.—In accordance with the following equations, phosphorus pentoxide unites with water to yield three different acids—

$$P_2O_5 + H_2O = 2HPO_3$$
$$P_2O_5 + 2H_2O = H_4P_2O_7$$
$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

The first acid is monobasic, and is called *metaphosphoric acid*; the second is tetrabasic, and is called *pyrophosphoric acid*; and the third, finally, is tribasic, and is called *orthophosphoric acid*, or ordinary phosphoric acid. When phosphoric acid is spoken of without any prefix, orthophosphoric acid is always meant.

Of the three acids, the last is by far the most important. In nature, compounds of it alone are found, and the other acids pass spon-aneously, in aqueous solution, into the orthophosphoric acid, just as the different forms of sulphur at the ordinary temperature all pass ultimately into rhombic sulphur as being the most stable form.

Orthophosphoric acid is obtained by dissolving phosphorus pentoxide in water and allowing the solution to stand for a length of time, preferably in the heat. The least stable form, metaphosphoric acid, is first formed, and this gradually passes into the stable form. The acid is obtained more conveniently by oxidising white phosphorus with dilute nitric acid. The phosphorus dissolves with evolution of nitric oxide; the phosphoric acid which is formed can be readily freed from the excess of nitric acid and its reduction products, by strongly concentrating and heating.

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[1] This decomposition has not yet been experimentally proved, since there is no eagent by which nitrogen pentoxide can be detected in presence of nitric acid. In the use of sulphuric acid, however, the anhydride of which can be recognised by its olatility and the corresponding fuming in the air, the decomposition can be easily bserved (p. 287).

Orthophosphoric acid is obtained in this way as a viscous liquid which crystallises only slowly and with difficulty. The melting point of the pure acid is 42°; the melting point is lowered by the presence of water, and likewise, also, by the presence of the less hydrated acids. This is due to the general fact that the melting point of every substance is lowered by the presence of a foreign substance.

Impure phosphoric acid is obtained from bone-ash. The bones of the mammals consist partly of the calcium salt of orthophosphoric acid and partly of organic nitrogeneous matter which, on heating with water passes into glue. If the bones are heated in the air, they first become black owing to the carbonisation of the organic substances; on continuing the heating, the charcoal burns and the calcium phosphate is left in the form of white masses retaining the outward form of the bones. This residue is called bone-ash.

If powdered bone-ash is mixed with dilute sulphuric acid, there occurs a reaction of the kind described on p. 290. Calcium sulphate is a difficultly soluble salt, and for this reason it is formed from the sulphuric acid and calcium phosphate, and phosphoric acid is formed at the same time. On filtering the mass, the aqueous solution of phosphoric acid which is formed is separated from the precipitate of calcium sulphate.

Since, however, this salt is not over-difficultly soluble, a certain amount of it remains in the solution. Since, also, bone-ash is not pure calcium phosphate, and some of the impurities also form soluble compounds under the action of sulphuric acid, the phosphoric acid obtained in this way is not pure, although pure enough for many technical purposes.

As can be gathered from this description, phosphoric acid is soluble in water. Indeed, it is so soluble that its solubility has hitherto never been determined. Even small amounts of water lower the melting point of phosphoric acid below room temperature, and thus convert it into a solution which, certainly, contains only a small quantity of the solvent, *i.e.* of water.

The aqueous solution reacts acid to litmus, and has a pure and pleasantly acid taste. Its electrical conductivity is comparatively slight; one mole of phosphoric acid dissolved in 10 litres of water contains only a quarter as much hydrion as an equally dilute hydrochloric acid solution.

Phosphoric acid, is a tribasic acid and can therefore form three series of salts in which one, two, or three combining weights of hydrogen are replaced by metals. Since there are two different acid salts and one normal salt, these are distinguished by stating in Greek numerals how many combining weights of hydrogen are replaced. Thus, monopotassium phosphate is the salt KH_2PO_4, disodium phosphate is Na_2HPO_4, and tri-silver phosphate is Ag_3PO_4. In nature, only salts of the last type, or normal salts, occur.

On attempting to neutralise an aqueous solution of phosphoric acid with caustic soda with the aid of litmus, no sharp transition is obtained. Instead of the three combining weights of caustic soda which would be required for the formation of the normal salt according to the equation $H_3PO_4 + 3NaOH = Na_3PO_4 + 3H_2O$, less than two are required to produce an alkaline reaction, and the blue coloration of litmus appears gradually, so that no definite moment can be given at which the liquid reacts neutral. Also, the amount of caustic soda depends on the dilution; the more dilute the solution, the sooner does the blue colour appear.

The cause of these phenomena is the difference in the dissociation of the three hydrogens of phosphoric acid. The dissociation $H_3PO_4 = H^{\cdot} + H_2PO_4{}'$ occurs comparatively easily and in measurable amount. The further dissociation $H_2PO_4{}' = H^{\cdot} + HPO_4{}''$ takes place only in very slight degree, and the third dissociation, $HPO_4{}'' = H^{\cdot} + PO_4{}'''$, is exceedingly slight. When, therefore, a normal salt, *e.g.* the solution salt Na_3PO_4, is dissolved in water, the corresponding ion $PO_4{}'''$ cannot exist, but acts on the water of the solvent in the sense of the equation $PO_4{}''' + H_2O = HPO_4{}'' + OH'$. Hydroxidion is produced, and the liquid must, therefore, react alkaline. In other words, we have here again a case of hydrolysis (p. 247).

The divalent ion, $HPO_4{}''$, also experiences in slight degree a similar transformation in aqueous solution, $HPO_4{}'' + H_2O = H_2PO_4{}' + OH'$, so that the disodium phosphate also undergoes slight hydrolysis, and therefore exhibits a feeble alkaline reaction. This is, however, much feebler than in the case of the normal salt.

Since these different equilibria exist side by side, and are also dependent on the temperature and the dilution, it is clear that on neutralisation the hydrion does not suddenly disappear, as in the case of strong acids, but its amount diminishes gradually and continuously. For this reason, no sudden but only a continuous change of colour occurs when litmus is present.

The heat of formation of the trivalent phosphanion $PO_4{}'''$, amounts to 1246 *kj.*; that of the divalent hydrophosphanion, PO_4H'', 1277 *kj.*

Pyrophosphoric Acid.—If orthophosphoric acid is carefully heated to 250°, it loses water and is converted into pyrophosphoric acid, $H_4P_2O_7$. This process takes place in accordance with the equation

$$2H_3PO_4 = H_4P_2O_7 + H_2O.$$

A sure means of obtaining pure pyrophosphoric acid is to he such salts of orthophosphoric acid as contain just enough hydrogen t yield a residue of pyrophosphate. This happens in the case of th salts in which two hydrogens are replaced by metal, *e.g.* ordinary d sodium phosphate. If this salt is heated, the following reaction tak place—

$$2HNa_2PO_4 = Na_4P_2O_7 + H_2O.$$

The free pyrophosphoric acid can be obtained in aqueous solutio from the pyrophosphate thus formed, by converting the latter into th difficultly soluble lead salt and decomposing this with sulphurette hydrogen.

Unlike pyrosulphuric and pyrosulphurous acids (pp. 291 and 282 pyrophosphoric acid retains its state in aqueous solution for a tim and changes only slowly into orthophosphoric acid. The latter repr sents the stable state to which the aqueous solution of the acid und all circumstances approaches. The velocity with which this conditio of equilibrium is reached, depends on the temperature and the co centration of the hydrion in the solution ; the latter accelerates th transformation catalytically. For this reason, the transformatio takes place much more quickly if nitric acid is added to the solutio and the concentration of the hydrion thereby increased.

Apart from the composition of the salts, pyrophosphoric acid is di tinguished by various reactions from the ortho-acid. As is appare from the formula, it is tetrabasic, and forms, accordingly, four series salts. The neutral or normal salts contain two combining weights a monovalent metal or monovalent cation to one combining weight phosphorus, whereas normal salts of orthophosphoric acid contain thre combining weights of a monovalent cation to one of phosphorus.

To distinguish the two acids, silver nitrate is added to the sol tion. If orthophosphoric acid, or generally, the ion PO_4''', be presen a yellow silver salt of the composition Ag_3PO_4 is precipitated ; pyr phosphates, or the ion P_2O_7'''', yield, on the other hand, a whit precipitate of the composition $Ag_4P_2O_7$. By means of this reactio also, one can observe the slow transformation of a solution of pyr phosphoric into orthophosphoric acid.

Metaphosphoric Acid.—On heating orthophosphoric acid mo strongly, it passes into metaphosphoric acid, which analysis shows to hav the composition HPO_3. Its composition is, however, not represente by the simple formula but by a multiple formula $(HPO_3)_n$, where n i a whole number. There are various metaphosphoric acids which ar probably distinguished from one another by the difference in the valu of n ; the chemistry of these compounds, however, has as yet bee cleared up only to a rather small extent.

Metaphosphoric acid obtained in the above manner forms a glass like mass which, at a moderately high temperature, melts to a viscou iquid, and, on cooling, forms an amorphous solid. The "glacial" hosphoric acid of commerce is metaphosphoric acid. It dissolves in vater, yielding an acid liquid whose reactions are different from those f the other phosphoric acids. It gives, indeed, like pyrophosphoric cid, a white silver salt, but has the further property of precipitating lbumen, a property which is not possessed by the other phosphoric cids. A solution of metaphosphoric acid is used, therefore, to detect he presence of albumen, *e.g.* in urine. For this purpose, the solution f the acid must be freshly prepared since, on keeping, it is slowly con-erted into orthophosphoric acid.

For this transformation, the same general remarks hold as were ıade for the corresponding transformation of pyrophosphoric acid. 'yrophosphoric acid has, however, not been detected as an intermediate roduct, although, on theoretical grounds, it is probable that it is ıdeed formed.

Also when phosphorus pentoxide is dissolved in water, metaphos- horic acid is formed as the first product, and not the form which is ıost stable under these circumstances, viz., orthophosphoric acid, in ccordance with the general law of the first appearance of the less able forms.

Chlorides of Phosphoric Acid.—If orthophosphoric acid were ıpable of further taking up one combining weight of water, a penta- ısic acid would be produced: $H_3PO_4 + H_2O = H_5PO_5$ or $P(OH)_5$. If ıe imagine all the hydroxyls of this acid to be replaced by chlorine, e obtain PCl_5, the phosphorus pentachloride already described. As matter of fact, the chloride, when decomposed with water, yields ıosphoric acid along with hydrochloric acid: $PCl_5 + 4H_2O = H_3PO_4 +$ HCl.

Besides this chloride, there is also known the chloride of ortho- ıosphoric acid, if the formula of this is written $PO(OH)_3$. This loride has the composition $POCl_3$, and is usually called phosphorus ychloride.

Phosphorus oxychloride is a colourless liquid, which has the density 68, and which boils at 107° and fumes in the air. It is violently composed by water to hydrochloric and orthophosphoric acids: $OCl_3 + 3H_2O = H_3PO_4 + 3HCl$.

The compound is prepared by the action of small amounts of ıter on the pentachloride: $PCl_5 + H_2O = POCl_3 + 2HCl$. In place water, numerous other compounds can be used in which oxygen d hydrogen are present. If such a compound is represented by e formula R . OH, the reaction takes place according to the equation . $OH + PCl_5 = R . Cl + POCl_3 + HCl$. In the case of hydroxyl com- unds, this reaction occurs so readily and regularly that it is used to termine whether hydroxyl should be assumed in any given com- und or not. In organic chemistry, especially, phosphorus penta- loride is used in this way as a reagent for hydroxyl.

As an example of this action, it may be cited that sulphuric aci on being treated with phosphorus pentachloride, yields chlorosulphoni acid or sulphuryl chloride (p. 302), according to the proportion used. The reactions take place in accordance with the equation $SO_2(OH)_2 + PCl_5 = HOSO_2Cl + HCl + POCl_3$ and $H_2SO_4 + 2PCl_5 =$ $SO_2Cl_2 + 2POCl_3 + 2HCl$.

Similarly, nitryl chloride is formed by the action of the pent chloride on nitric acid: $NO_2OH + PCl_5 = NO_2Cl + HCl + POCl_3$.

Another preparation of phosphorus oxychloride is from phosphoru pentachloride and pentoxide. It takes place according to the equatio $P_2O_5 + 3PCl_5 = 5POCl_3$, if the two substances are mixed in the prop proportions and heated in a sealed tube.

* The method of allowing substances to act on one another i sealed glass tubes is employed when it is desired to use a fairly hig temperature above the boiling point of one of the reacting substanc under atmospheric pressure. The necessity for a higher temperatu occurs when the reaction does not proceed quickly enough at low temperatures. Even in the case of substances sealed up in glass tube which must be made of strong glass and carefully sealed off, th volatile substance, it is true, will partially vaporise; the pressure i the interior of the tube, however, thereby rises, and with it also th boiling point, so that the greater part of the substance does not pas into vapour.

* The pressure hereby produced has, in general, only a sligh influence on the chemical reaction; the essential point is the possibilit of raising the temperature without the substance evaporating.

The heat of formation of phosphorus oxychloride is 611 *kj*.

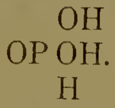
Phosphorous Acid.—When phosphorus trichloride is decompose with water, there is formed the compound PO_3H_3, which has aci properties and is called phosphorous acid.

The reaction which leads to the formation of phosphorous acid i represented by the equation $PCl_3 + 3H_2O = P(OH)_3 + 3HCl$. It take place with great rise of temperature, and this can easily effect a furthe decomposition of the phosphorous acid. It is, therefore, expedient t use concentrated hydrochloric acid in place of pure water. Th hydrogen chloride formed will then not be dissolved but will escap as a gas, and the heat of reaction will thereby be diminished by th amount of the heat of solution of hydrogen chloride. The resultin acid liquid is freed from the excess of hydrochloric acid by evaporatio on the water-bath, and the pure phosphorous acid, melting at 74 crystallises out from the liquid on cooling.

Since phosphorous acid contains one combining weight less oxyge than phosphoric acid, it can, by taking up oxygen, pass into the latte it then acts as a reducing agent. On being heated, it acts in this wa on itself, whereby a portion is reduced to hydrogen phosphide $4H_3PO_3 = 3H_3PO_4 + PH_3$. We have here assumed the formation orthophosphoric acid ; as a matter of fact, this simultaneously loses water and passes into metaphosphoric acid. The corresponding change in the equation can be easily made. The hydrogen phosphide which is formed takes fire at the temperature of decomposition, and burns with a greenish flame.

Phosphorous acid also behaves as a reducing agent in aqueous solution, and withdraws oxygen and halogen from many substances. Thus, the silver and mercury salts, more especially, are reduced to the metals, which are precipitated from the solution. This reaction is used more especially for the detection of dissolved nercury compounds.

In neutralising phosphorous acid with the aid of litmus or any ther indicator, no sharp transition is obtained. The liquid becomes lue before the second equivalent of caustic soda or potash has been dded, so that, at most, only two combining weights of hydrogen of he acid can be replaced by metals in aqueous solution, and even in he solid state, no salts of phosphorous acid are known in which more han two combining weights of hydrogen are replaced. Phosphorous cid is, therefore, regarded as a dibasic acid, and its formula written I_2PO_3H.

* This behaviour can be expressed by assuming that the two eplaceable hydrogens are joined to oxygen to form hydroxide, hereas the third is united directly to phosphorus. This would ive the formula  $OP\begin{matrix}OH\\OH.\\H\end{matrix}$ According to this, phosphorous acid ould be a derivative of phosphoric acid, in which one hydroxyl replaced by hydrogen.

* The circumstance, however, that phosphorous acid is formed uite smoothly by the action of water on phosphorus trichloride, eaks against this. The formation of the acid by water is a pical reaction of the acid chlorides; these, on the other hand, e derivatives of the acids formed by the replacement of hydroxyl y chlorine. According to these reactions, phosphorus trichloride ught to be the chloride of phosphorous acid, and this ought, there-re, to have the formula $P(OH)_3$.

* These contradictory views are not irreconcilable. It is not cessary that all the hydrogen which is present in hydroxyl should replaceable by metals. According to what was said on p. 268, the adual dissociation of a polybasic acid must take place with greater fficulty with each successive step. We have here a case where the t stage is so difficult to attain that, under normal conditions, no placement of the third hydrogen by metals occurs, and the formula $OH)_3$ can be quite well reconciled with the dibasic nature of phos-orous acid. If it is desired to give expression to this, the formula n also be written $H_2PO_2(OH)$.

* The foregoing discussion furnishes an example of how attempts are made to express the so-called "constitution" of a compound by the way in which the formula is written. By this is meant that the formula is written in such a way as to give expression to the most important reactions of the substance in question, so that these can be easily read out of the formula.

* The means adopted for this consists in writing those elements which are often eliminated together in such a way that they appear side by side in the formula; they are sometimes still further separated from the other elements by means of a bracket or a dot.

* Such a separation can, for example, be very well carried out in the case of salts in respect of the two ions, and the formula of ammonium nitrate is, therefore, not written $N_2H_4O_3$, which represents the total composition, but in the form $NH_4 . NO_3$, to show that the salt when dissolved in water dissociates into the ions $NH_4^{\cdot}$ and NO_3'.

* In the case of the polybasic acids, which can form several ions, this separation causes some difficulty. In such cases it is carried out in such a way that all the hydrogen which could form hydrion if the dissociation were complete, is separated; thus, phosphoric acid is written H_3PO_4; in this way all the three hydrogens are made to appear as ions, although, in aqueous solution the third hydrogen is dissociated only to a very slight extent. In the case of phosphorous acid, only two hydrogens are regarded as ions, although we are probably dealing only with a difference of degree, and not with an essential difference.

* The demand for a universally valid formula can be still less met where we are dealing with oxy-acids which can, on the one hand, split off hydrion, and, on the other hand, when water is excluded, act as hydroxyl compounds. This is the case, for example, with sulphuric acid. This difficulty is overcome by employing different formulæ, according to the reaction to which it is desired to give expression. Accordingly, sulphuric acid, as acid, is written H_2SO_4, or $H_2 . SO_4$, as hydroxyl compound, however, $SO_2(OH)_2$. In other words, the "constitution" of sulphuric acid cannot be represented by a single formula, and use is therefore made of more than one, according as they are required.

* One might, perhaps, also unite the two formulæ by using the latter and stating the rule that the hydrogen attached to the oxygen in hydroxyl is specially capable of being split off as hydrion. We would then, however, come back to the contradiction of phosphorous acid, apart from the fact that no splitting off of hydrogen can be detected in the case of the basic hydroxides.

* The question must be asked, why it is that these relations give rise to such changing formulation, whereas many other relations could be established with definiteness and free from contradiction. The answer is that it is here a question of representing very varied

relations, the laws of which depend on many more variables than are expressed in the chemical formula. The task consists, indeed, of giving a summary of all the transformations which one substance can undergo with others; these transformations, also, so far as their result is concerned, are not quite definite, but depend to a large extent on external conditions, such as temperature and pressure or concentration. All these diversities cannot, of course, be represented by the simple means of the relative arrangements of the elementary symbols, even with the assistance of space, and a "constitutional formula" must therefore always remain one-sided and be limited to the representation of definite relations which have a special importance from their frequent occurrence.

By the very moderate oxidation of phosphorus in a slow current of air, a white substance is obtained, which differs from the phosphorus pentoxide by its low melting point (22·5°), and its volatility (boiling point 173°). Analysis shows it to contain three combining weights of oxygen to two of phosphorus; determinations of the vapour density, however, give the molar weight as 220, and lead, therefore, to the formula P_4O_6. It is the anhydride of phosphorous acid, for

$$P_4O_6 + 6H_2O = 4H_3PO_3.$$

Hypophosphorous Acid.—The formation of the salts of this acid from phosphorus and a solution of caustic soda or potash, has already been mentioned under hydrogen phosphide (p. 355). It takes place according to the equation

$$4P + 3NaOH + 3H_2O = 3NaPO_2H_2 + PH_3,$$

and the salt produced is found in the solution. For the purpose of preparing the acid, barium hydroxide is used; this acts in a quite similar way, and gives rise to a solution of barium hypophosphite. The salt is obtained pure by evaporation and recrystallisation, and is then decomposed with the requisite amount of sulphuric acid. From the aqueous solution, the free acid is obtained by careful evaporation as a crystalline mass, which melts at 17°, and is very soluble in water.

Hypophosphorous acid has the composition H_3PO_2; of the three combining weights of hydrogen, however, only one can be replaced by metals, so that the acid is monobasic. To indicate this, it may be written $H . PO_2H_2$.

In its other reactions, hypophosphorous acid is very similar to phosphorous acid. Like it, it is a reducing agent which precipitates noble metals from their solutions; also, on being heated, it evolves hydrogen phosphide, which immediately ignites.

The salts are almost all soluble in water, so that none of them can be used for the identification of the acid.

An oxygen compound of phosphorus, which would correspond t the anhydride of this acid and would have the formula P_2O, is not known.

Hypophosphoric Acid.—In the acid liquid which phosphoru yields on being left exposed to moist air, there is contained, beside phosphoric and phosphorous acids, a compound which is intermediat between these two; this is called hypophosphoric acid, and has th composition $H_4P_2O_6$. As can be seen from the formula, it is tetrabasic acid.

The acid is obtained from the above mixture by partly neutralisin it with caustic soda and allowing to stand; the acid sodium sal $Na_2H_2P_2O_6$ then slowly separates out, and this is converted into th sparingly soluble lead salt which can be decomposed by means o sulphuric acid or sulphuretted hydrogen.

Hypophosphoric acid behaves, in general, similarly to phosphorou acid, but its reducing properties are less pronounced. On being heated the free acid, like all the lower acids of phosphorus, passes int phosphoric acid, with simultaneous evolution of hydrogen phosphide which partly burns and partly decomposes into hydrogen and re phosphorus.

Sulphur Compounds of Phosphorus.—When white phosphoru and sulphur are brought together, yellowish liquids are obtained whic fume in the air and are readily inflammable. These were for a lon time regarded as compounds of phosphorus with sulphur, but it ha been found that they are only solutions of the one element in th other. Since the melting point of every solid substance is lowered b the solution of another substance in it, this must also be the case wit phosphorus when sulphur is dissolved in it. The impression tha chemical combination had taken place here, was caused only by th fact, that the melting point of the phosphorus, which, for the pur substance, is 44°, is hereby depressed to below room temperature, s that the solutions comparatively rich in sulphur remain liquid.

Compounds of the two elements, however, corresponding to th oxygen compounds of phosphorus, are obtained by allowing them t act on one another at a moderately high temperature. With whit phosphorus so much heat is thereby developed that dangerous expl sions can occur; if red phosphorus, which contains much less energ is employed, the heat development is correspondingly less, and th process can be easily kept under control.

The two substances are mixed in the proportions corresponding t the formulæ P_3S_6 and P_2S_5, the mixture placed in a glass flask, and th latter heated at one spot. Combination then proceeds rapidly, bu without explosion, through the whole mass. The resulting compoun is, at first, liquid, but soon solidifies to a yellow-grey crystalline mas The two compounds P_3S_6 and P_2S_5 can scarcely be distinguished b their appearance. The yellow-grey colour is due to contaminatio with red phosphorus; the pure compounds are yellow, crystalline masses which look like sulphur, but are paler in colour.

The compounds do not take fire spontaneously in the air; on being heated, they burn to sulphur dioxide and phosphorus pentoxide. They smell of sulphuretted hydrogen, because they are converted by the water vapour in the air into this gas and phosphoric or phosphorous acid: $P_2S_5 + 8H_2O = 2H_3PO_4 + 5H_2S$. They act similarly on compounds containing hydroxyl, and convert these into the corresponding sulphur compounds.

Besides these compounds, there are still two other sulphides of phosphorus, the composition of which is represented by the formulæ P_4S_3 and P_4S_7. They can be obtained pure by melting the two elements together in the proper proportions and distilling under reduced pressure.

In view of the analogous composition of phosphorus pentasulphide and the corresponding oxide, it may be asked if acids cannot be derived from the sulphide, as can be done in the case of the oxide. It is very probable that there exists a whole series of acids corresponding to the oxygen acids of phosphorus, and containing sulphur in place of oxygen. They are, however, very slightly stable, since they are converted by water into the corresponding oxygen compounds, with evolution of sulphuretted hydrogen. We shall, therefore, not enter nto a discussion of these compounds, especially as similar compounds, only more stable and better characterised, are met with in the case of arsenic, and will be then discussed.

Great stability, however, is possessed by phosphorus sulphohloride, the sulphur compound corresponding to phosphorus oxyhloride. This has the composition $PSCl_3$, and can be obtained by heating phosphorus trichloride with sulphur. It is also formed by he action of phosphorus pentachloride on sulphuretted hydrogen. t is a colourless liquid which boils at 125°, and is decomposed by water with much less violence than the oxychloride. In the decomosition there are formed phosphoric and hydrochloric acids and ulphuretted hydrogen: $PSCl_3 + 4H_2O = H_3PO_4 + 3HCl + H_2S$.

Valency.—The fact that in sulphuric acid two combining weights f hydrogen are present to one combining weight of sulphur, can e expressed, as has been done, by designating the anion SO_4'' as divalent." Likewise, the anion of a tribasic acid will be called trialent, and so on.

On the other hand, besides the monovalent cation hydrogen nd the other monovalent cations, which each replace one combining eight of hydrogen, there are others, of which one combining weight n take the place of two or three, or even more, combining weights hydrogen. Accordingly, there are mono- and polyvalent cations.

* The question may be asked, why are the combining weights of the elements not determined in such a way that only monovalent

ions require to be assumed? The answer is that there would the arise a contradiction of the results obtained by the determinations o the molar weights. Thus, calcium has been designated as a divalen cation, because the amount of calcion in the compound $CaCl_2$ exercise the same influence on the freezing point as the amount of potassio contained in the compound KCl.

* A second reason against carrying out the formulation with onl monovalent ions is found in the circumstance that there are a numbe of ions (some of them elementary ions) which, while preserving th same composition, have, according to circumstances, different valenc while their molar weight remains the same. This is the case, *e.g.*, wit iron, which can form di- and trivalent ions, both of which have th same molar weight expressed by the symbol Fe.

Starting, then, with any acid H_nA, if n combining weights hydrogen can be replaced by metals, the anion A will be calle n-valent. Likewise, a cation of which, in the displacement hydrogen from an acid, one combining weight replaces m combinin weights of hydrogen, will be called m-valent. This calculatio depends on measuring the valency by the unit of hydrogen. A experience has shown, no smaller unit is necessary, for there is n anion of which one normal weight would contain less than one combining weight of hydrogen, and no cation of which one combinin weight would take the place of less hydrogen.

From this, it at the same time follows that the valency of th anions and the cations is determined in such a way that in every sa both must have the same value. It is not necessary that an n-vale cation shall always be united only with an n-valent anion; it sufficient if the *sum* of the valencies of the cations is equal to tha of the anions. To bring this about, the number of ions which uni together must vary with their valency. Thus, a divalent catio requires two monovalent anions, and if a trivalent anion has combine with a divalent cation, two combining weights of the form must enter the salt with three combining weights of the second, order that the sums of the two valencies shall be equal, viz., 6.

Extension of the Conception of Valency.—Whereas, in th case of salts, the conception of valency admits of no doubt, since it possible by means of Faraday's law (p. 194) to control it experimentall even independently of chemical considerations, no such sure foundati exists for the attempt which has been made to extend this conceptio to non-saline substances. Nevertheless, so many regularities ha been found to exist even in these departments of its application, th a short consideration of them will be useful. We shall at once rema that it is in *organic* chemistry that these views have been of greate profit. This may serve as an explanation why these consideratio which play a comparatively small rôle in inorganic chemistry, a discussed here.

On comparing the composition of the hydrogen compounds of the elements hitherto described, we obtain the following summary :—

Halogens	HH, HF, HCl, HBr, HI.
Oxygen group	H_2O, H_2S, H_2Se, H_2Te.
Nitrogen group	H_3N, H_3P.

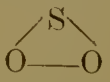
If hydrogen be again taken as the standard by which the combining power of the different elements is judged, the halogens can be designated as monovalent, the elements of the oxygen group as divalent, and those of the nitrogen group as trivalent. We shall presently see that carbon and the related elements can be regarded as tetravalent.

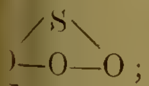
If we again put forward the requirement that every compound shall be separable into two parts, in which the sums of the valencies present on each side are equal, this requirement can be tested in the formulæ of the compounds by attaching one stroke to the symbols of the monovalent, two strokes to those of the divalent, and three strokes to those of the trivalent elements. The above demand will be fulfilled if the formula of the compound can be so written that all the elementary symbols are united by strokes, and the number of strokes ending in each symbol agrees with the valency of the element which it denotes.

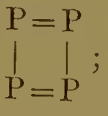
Thus, the elements of the halogen series will have to be written with one stroke: H— ; Cl— ; Br— ; I— ; F—; those of the oxygen series with two strokes : —O— ; —S— ; —Se— ; —Te— ; those of the nitrogen series with three strokes : —N= ; —P= .

If we test the compounds hitherto described from this point of view, we find that the condition, although often, is still not always, fulfilled. In the case of the following formulæ, certainly, it can be done :—

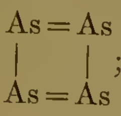
H—H ; Cl—Cl ; Br—Br ; I—I ; F—F ; H—Cl ; H—Br ; H—I ; H—F ; I—Cl ; O=O ; S=S ; Se=Se ; Te=Te ; H—O—H ; H—S—H ; H—Se—H ; H—Te—H ; Cl—O—Cl ; Cl—O—H ; Cl—O—O—H ; Cl—O—O—O—H ; Cl—O—O—O—O—H ;

Cl—S—S—Cl ; Cl—S—Cl ; Cl—Se—Cl ; Cl—Te—Cl ;  ;

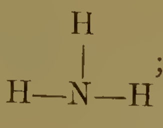
 ; H—S—O—O—O—H, or H—O—S—O—O—H ; H—S—O—O—O—O—H, or H—O—S—O—O—O—H, or H—O—O—S—O—O—H ; and similarly, the remaining oxyacids of sulphur, selenium, and tellurium.

N≡N ; 

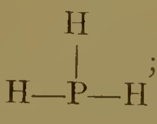
$$\begin{array}{c} P=P \\ |\quad\;\; | \\ P=P \end{array}$$

; 

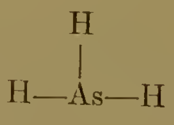
$$\begin{array}{c} As=As \\ |\quad\;\;\; | \\ As=As \end{array}$$

; 

$$\begin{array}{c} H \\ | \\ H—N—H \end{array}$$

; 

$$\begin{array}{c} H \\ | \\ H—P—H \end{array}$$

; 

$$\begin{array}{c} H \\ | \\ H—As—H \end{array}$$

.

On the other hand, it is not possible in the case of the compounds

$$SCl_4,\ SeCl_4,\ NH_4Cl,\ PCl_5,\ PF_5,\ NO,\ NO_2,$$

and many others.

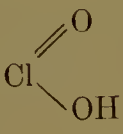
Various attempts have been made to overcome these contradictions, chiefly by assuming that the elements can have different valency. Thus, the above sulphur and selenium compounds can, evidently, be referred to a tetravalent sulphur, and the nitrogen and phosphorus compounds, at least partially, to a pentavalent form of the corresponding elements. Nitric oxide and nitrogen peroxide, however, would require a di- or tetravalent nitrogen.

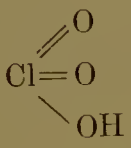
That which forms the basis of these considerations, is the fact that the different compounds of a given element can be arranged in groups which are more closely related to one another, *i.e.* which can be easily converted into one another and give, under similar conditions, similar reactions. The number of these groups or types is different in the case of the different elements; whereas some, *e.g.* carbon, have only a few groups with a very large number of members, in the case of others the number of the groups is large but that of the representatives in each group small. By fixing these groups or types in one's memory, a clearer view of the existing diversities can, in any case, be obtained than by merely writing these down in a list.

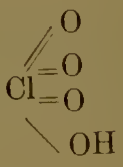
For the present, the following groups may be noticed :—

Hydrogen is monovalent, oxygen is divalent.

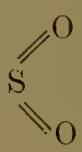
The halogens are monovalent in the hydrogen acids and in the salts derived from these. Further, there are characterised the tri-, penta-, and heptavalent types of the oxyacids, of which the middle one is the most important, and which are expressed in the following formulæ :—

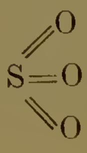




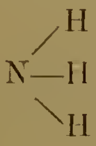


The elements of the sulphur group are divalent in the hydrogen acids and the corresponding salts. Further, a tetra- and a hexavalent type can be recognised, the representatives of which are sulphurous and sulphuric acids, or their anhydrides—

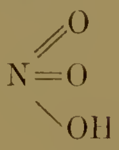




Nitrogen and phosphorus (along with the related elements to be treated later) are chiefly tri- and pentavalent. Types: ammonia and nitric acid—



$\mathrm{N}\begin{array}{l} /\mathrm{H} \\ -\mathrm{H} \\ \backslash\mathrm{H} \end{array}$



$\mathrm{N}\begin{array}{l} /\!\!/\mathrm{O} \\ =\mathrm{O} \\ \backslash\mathrm{OH} \end{array}$

For certain purposes, which will come into prominence later, it is expedient to consider the above oxygen compounds all as partial anhydrides of hydroxyl compounds. Since oxygen is divalent, but hydroxyl monovalent, the adopted valency becomes more prominent by this way of writing the formulæ.

Thus, in the case of the halogens, *e.g.* in the case of chlorine, we have

Hypochlorous acid	$Cl(OH)$
Chlorous acid	$ClO(OH) = Cl(OH)_3 - H_2O$
Chloric acid	$ClO_2(OH) = Cl(OH)_5 - 2H_2O$
Perchloric acid	$ClO_3(OH) = Cl(OH)_7 - 3H_2O.$

In the case of sulphur and its group, we have

Sulphurous acid	$SO(OH)_2 = S(OH)_4 - H_2O$
Sulphuric acid	$SO_2(OH)_2 = S(OH)_6 - 2H_2O.$

In the nitrogen series, finally, there are

Nitrous acid	$NO(OH) = N(OH)_3 - H_2O$
Nitric acid	$NO_2(OH) = N(OH)_5 - 2H_2O.$

By means of this view the fact, *e.g.* that the tribasic phosphoric acid and the monobasic nitric acid belong to the same type, becomes clearer than from the mere consideration of their formulæ—

$$H_3PO_4 = P(OH)_5 - H_2O$$
$$HNO_3 = N(OH)_5 - 2H_2O.$$

Even if these types do not by any means exhaust all the cases, still they allow of a review of the most important compounds, and have their value on that account.

CHAPTER XVI

CARBON

General.—Carbon is one of the most important elements in respect both of the variety and wide distribution of its compounds and of the importance which these have in nature as well as in the arts. Although oxygen, hydrogen, and nitrogen are never failing constituents of living or organised structures, still carbon is frequently called the organic element *par excellence*, because it is on the combining relations exhibited by this element that the diversity of the substances of the organic kingdom most essentially depends.

But the pre-eminent importance of carbon is due not only to its being a constituent of the substances of which the structures of living things are built up, but much more to its being the carrier of the supply of energy which is expended in vital action. For a similar reason, carbon is of importance in the arts, for by far the greatest part of the chemical energy which is set in motion for the accomplishment of the most diverse ends is derived from the chemical transformations of carbon.

Into a discussion of this side of the chemistry of carbon, however, we can enter only after the compounds have been described which carbon forms with other elements. This, in turn, must be preceded by a description of carbon itself.

Elementary carbon occurs in three different forms, which exhibit relationships to one another similar to those found in the case of sulphur or phosphorus. It exists in two crystalline forms and also in an amorphous state. The different varieties of amorphous carbon are usually, but probably incorrectly, classed together as one kind. Indeed, there are important reasons for thinking that there are several kinds of amorphous carbon, each possessing different properties, but none of which are known in the pure state.

That which is called *charcoal* is amorphous carbon in a more or less pure state. On heating organic substances, *e.g.* substances derived from organisms, especially plants, and containing carbon, a residue of this element is generally obtained, whereas the other elements present especially oxygen and hydrogen, escape in the form of water and as lower carbon compounds of these elements. Moreover, the residue contains any non-volatile substances which may be present, as well as residual quantities of hydrogen and oxygen, which are larger in amount the lower the temperature of carbonisation.

In the charcoal produced, the structure of the material can in some cases, *e.g.* when obtained from wood, be recognised; wood charcoal exhibits every cell of the wood well preserved. This is due to the fact that at the temperatures which are reached under these conditions, carbon is an infusible substance. If the original material has also this same property of infusibility, as is the case with the substance forming the cell-walls of wood, the form is well retained on carbonisation. In other cases, where the original material liquefies either before or during carbonisation, *e.g.* in the case of sugar, the charcoal which is obtained has the appearance of a mass which has been fused; this, however, is due only to the fact that sugar, not carbon, is fusible.

Sugar charcoal is much purer than wood charcoal, because in it the presence can easily be avoided of non-volatile impurities which are present in the case of wood charcoal, and which, on complete combustion, remain behind as a grey powder, the ash.

Soot is a still purer form of carbon. This is obtained by the combustion, in a small supply of air, of volatile compounds of carbon and hydrogen, of which there are a large number. The hydrogen then combines with the oxygen present, and the carbon is deposited and can be collected in the form of a very fine and light powder. Small quantities of hydrogen compounds which it still contains can usually be got rid of by igniting it with exclusion of air.

The properties of this form of carbon are the well-known black colour, a small density, easy combustibility, small conductivity for heat and electricity, and a low degree of hardness.

All these properties, however, cannot be stated in definite numbers, but are found to vary to some extent, and that, indeed, in the following way. The higher the temperature to which the amorphous carbon was exposed, and the longer that temperature was allowed to act on the carbon, the greater are the density, hardness, conductivity for heat and especially for electricity, and the less is its combustibility. At the same time, the deep black colour passes into a gray one with a somewhat metallic lustre.

It has not yet been settled whether the cause of these changes is that the small particles of which the charcoal consists unite together at the high temperature to larger particles, or that there are different forms of amorphous carbon which occur mixed together in charcoal, the harder, more dense, and better conducting of which forms are increasingly produced at higher temperatures. The melting point of charcoal is certainly as high as 3000° or 3500°, the temperature of the electric arc, but it is quite possible that the general property of amorphous substances, of having no definite melting point, is present also in this case, and that, therefore, even at much lower temperatures, an incipient softening may occur which would lead to the formation of larger grains by the caking together of the smaller. In this way, the above-mentioned changes can be partially explained. It appears, however, especially in view of the increase of the hardness and conductivity, to be more appropriate to assume the existence of several forms of amorphous carbon, which differ from one another in the way described, and which in varying proportions make up ordinary charcoal.

Carbon retains the solid state with especial obstinacy. Only at the temperature of the electric arc, about 3500°, does softening and volatilisation occur. Further, there is scarcely a solvent which dissolves carbon to any great extent. The only better-known one is liquid iron, in which carbon dissolves to the extent of a few per cent at comparatively high temperatures, and from which it separates out when the metal solidifies. Under these conditions, however, carbon does not appear in amorphous form, but in the crystalline form of graphite, which will be described later.

When heated in the air, carbon unites with oxygen, and is converted into carbon dioxide.

The fossil charcoal occurring in nature, such as anthracite, coal, and brown coal, consists, it is true, chiefly of carbon, but it also contains hydrogen and oxygen along with small quantities of nitrogen, sulphur, and very varying amounts of ash, *i.e.* mineral admixtures of all kinds. The different sorts have all been formed in a similar way to wood charcoal, viz. from the remains of previous vegetation by the gradual loss of the other elements and the formation of a residue of carbon. This process has, however, taken place at a low temperature and required very long periods of time. This process of carbonisation has progressed furthest in the case of anthracite, which contains only quite small quantities of hydrogen; not so far in the case of ordinary coal, and least of all in the case of brown coal. The latter substances cannot be regarded as carbon in the strict sense; on the contrary, they consist of derivatives, of complex composition and certainly very rich in carbon, of the substances of which the original plant-structures were built up, or of mixtures of such substances with amorphous carbon.

On heating ordinary coal with exclusion of air, the hydrogen is removed in the form of carbon compounds. This process is carried out on the large scale for two purposes. On the one hand, coal rich in hydrogen is subjected to heating or "dry distillation," and the gases containing carbon which are produced are collected in order to be used, after purification, for illuminating or heating purposes. This manufacture of coal gas plays a very important part, since gaseous fuel possesses important advantages over the solid or liquid. We shall enter into this more fully later.

On the other hand, coal which is poor in hydrogen is also subjected to dry distillation in order to obtain in the residues a fuel which is almost free from hydrogen, and which in many cases, especially for metallurgical purposes, is to be preferred to that containing hydrogen. These coal residues are called coke, and are made on a very large scale. A point which is of essential importance here is that the greater portion of the sulphur present is removed in the carbonisation, so that in this respect also a purification is effected.

Absorption by Charcoal.—The porous and cellular character which amorphous charcoal frequently assumes, when produced from organic structures of a corresponding form, develops a property which is possessed, indeed, by all substances, but which, in this case, appears with especial distinctness. This is the power possessed by porous charcoal of absorbing dissolved and gaseous substances from mixtures, and so freeing these from certain components.

If, for example, wine, litmus solution, or similar coloured solutions are shaken with finely porous charcoal (the most suitable being bone charcoal, obtained by carbonising bones), and then filtered, the liquid passes through the filter either quite colourless, or, at least, considerably lighter in colour. Likewise, from turbid, impure, or evil-smelling water there is obtained, by filtration through charcoal, clear water which has lost its smell entirely or to a large extent. For such purposes of purification, charcoal is largely used both in the arts and in the laboratory.

The processes with which we are here dealing are called *absorption*, and depend on the fact that at the surface of contact between a solid body and a solution, a different concentration of the dissolved substance is produced from that in the interior of the solution. In many cases, the concentration of the dissolved substance at such bounding surfaces is greater than in the rest of the solution, but the opposite can also occur.

The cause which produces this action is of the same kind as that which effects wetting. The bounding surfaces between different bodies are, generally, the seat of a peculiar kind of energy which is called surface energy. The phenomena of surface tension or the phenomena of capillarity represent only a small portion of the actions of surface energy; indeed, this comes into operation in all cases where different bodies come together, or where surfaces of separation are present.

If, now, certain substances have the property of becoming specially concentrated at a bounding surface, they will be removed from a solution in which they are present when such bounding surfaces are formed in the solution. This is the case with charcoal and the above-mentioned colouring matters. A definite equilibrium is established between the portion in the solution and that absorbed on the charcoal, the greater part going to the charcoal.

This action depends, in the first place, on the nature of the dissolved substance, but to some extent also on the nature of the solid body. Substances of complex composition generally possess, to a comparatively much greater extent, the property of becoming concentrated at the bounding surfaces, whereas more simple substances remain chiefly in the solution. Since, now, most of the colouring matters which appear as unwelcome companion products in the preparation of organic substances have a very complex nature, they can be frequently removed from the solutions by this means. The method is employed with very good results, for example, in the sugar refineries, in order to so far decolorise the dark brown beet juice that white sugar can be obtained from it.

The same holds also for the malodorous products of decomposition of organic bodies, animal excremental matter, etc., which, on account of their complex nature, are also, as a rule, abundantly absorbed by charcoal.

Finally, what has just been said holds also for gas mixtures. Gases also condense to a more or less considerable extent on the surfaces of solid bodies, and again, the more complex and denser gases do so generally much more than the simple and light ones. The former can, therefore, also be removed more or less completely from mixtures with the other gases.

Since the action takes place at the bounding surface between the solid body and the liquid or the gas, it is proportional to the surface. The amount which 1 sq. cm. of surface can contain in this way is very small; in one special case (that of ammonia on glass) it has been found equal to $\frac{1}{25000000}$th gm. pro sq. cm. Even if in the case of other substances the number can become ten or a hundred times as great, still the amounts with which we are here dealing are always exceedingly small. To obtain measurable amounts, therefore, very large surfaces must be employed; for the absorption of one gram of ammonia a square surface of 50 metre side is necessary. Such large surfaces are found only in the case of very fine powders, or of very finely cellular structures.

This quality is possessed by bone charcoal, because bones contain, besides the organic matter of a gluey nature, large amounts of calcium phosphate. On carbonisation, the cellular structure is very completely preserved by means of this embedded matter, and if the calcium phosphate is removed by solution in hydrochloric acid, a fairly pure charcoal is obtained which for a given amount of substance possesses an exceedingly large surface, and therefore exhibits the phenomena of absorption with especial distinctness.

* If organic substances, *e.g.* sugar, which do not themselves yield on carbonisation a charcoal with largely developed surface, be mixed with calcium phosphate or similar infusible and readily removable salts, a strongly absorbing charcoal is obtained by the carbonisation of such mixtures, after removal of the admixed substance. In this case the

large development of surface has been artificially caused, and with it, also, the corresponding action obtained.

Another action with is connected with the one just described is the catalytic acceleration, especially of gas reactions, which is exerted by substances with largely developed surface. Thus, the oxidation of many substances by free oxygen is greatly accelerated when charcoal is present. Likewise, gases which under given conditions act only slowly on one another, can be made to act more quickly with the help of charcoal. In these cases, however, the actions of charcoal are greatly surpassed by the analogous actions of spongy platinum.

Graphite.—Graphite is a crystalline form of carbon. It occurs in nature as black-grey masses with a feebly metallic lustre, and crystallises in forms belonging to the hexagonal system; it is found in various localities, especially in Bohemia, Cumberland, and Siberia. It is distinguished from amorphous carbon by its greater density, its good conductivity for electricity, and the great difficulty with which it burns. It is possible to effect its combustion only by heating it to a bright red heat in a current of oxygen. From the denser and better conducting forms of amorphous carbon, it is distinguished by its very low degree of hardness. This circumstance makes it probable that amorphous carbon which has been strongly heated and has thereby become a conductor, does not owe this property to the formation of a certain amount of graphite, for such carbon becomes at the same time very hard and does not give a black streak as graphite does.

Graphite can also be obtained artificially by allowing carbon to crystallise out from fused metals. It has already been mentioned that this is best known in the case of iron, but there are other metals which dissolve small quantities of charcoal when heated, and from which the latter separates at lower temperatures in a crystalline form as graphite.

Graphite, also, must be divided into different groups which exhibit a somewhat different behaviour. It has, however, not yet been settled whether these differences may not perhaps be due only to mechanical differences, the one form consisting of innumerable laminæ laid closely together, while the other forms more coherent masses. We shall here, therefore, refrain from entering on a discussion of these differences.

Graphite agrees with amorphous carbon in its resistance to fusion, and volatilisation at comparatively high temperatures. It is used, therefore, for making crucibles which have to withstand especially high temperatures, and for this purpose it is mixed with some clay to act as binding material and then moulded. The slight combustibility of graphite allows of such crucibles being heated without special precautions even in the air.

Some further applications of graphite are due to its property of being split into thin scales. Lead pencils are made from graphite, the mass being finely powdered, and, by admixture with clay or other binding material, formed into the well-known thin rods, to which firmness is imparted by slight firing. According to the amount of substance added, the pencil has varying hardness.

Further, graphite is used as a lubricant, and this also depends on its easy disintegration into smooth scales. These fill up any unevenness in the rubbing surfaces and quickly form a smooth coating, which effects an easy gliding. Where it can be applied, graphite has the advantage over grease of being insensitive to differences of temperature.

Diamond.—A second crystalline form of carbon is the diamond. In contradistinction to the two other forms, diamond is transparent and colourless, but possesses the power of strong refraction and dispersion, so that, when cut into regular forms, it exhibits a considerable lustre and play of colours, to which its use as a gem is due. That it consists of pure carbon is seen from the fact that it yields on combustion carbon dioxide, and this also in exactly the same proportions as any other form of pure carbon.

Diamond crystallises in the regular system chiefly in octahedra, which often exhibit somewhat rounded edges. The property which is most important for its applications, is its great hardness. In this respect it is superior to all other naturally occurring substances, and also to most of those that can be artificially prepared. It is used for cutting glass, for drills for working in hard rock, for chisels used for turning very hard steel and emery discs, etc. A quickly rotating disc of tin-plate or of copper into which diamond splinters have been pressed, cuts glass and other hard substances with ease.

* According as it is desired to use the diamond for writing on or for cutting glass, differently formed pieces must be used. For writing, almost any point may be used which when properly held will scrape out splinters from the surface of the glass, and according to the sharpness of the point and the pressure employed, the finest lines can be drawn. For cutting glass, the diamond must have a chisel-shaped edge, which will cleave the glass; such a diamond cuts, therefore, only in one definite position, and must be held accordingly.

Diamonds occur rather rarely in nature, so that their price is high. Their artificial preparation has recently been successful, but has as yet yielded only microscopically small crystals. Diamonds are obtained by fusing iron which contains carbon and allowing this to fall in small quantities into water, so that it is suddenly cooled. If the iron is then dissolved, a small quantity of a crystalline dust is left whose density, hardness, resistance to the action of chemical agents, and combustion on heating, show it to be composed of diamond. In Fig. 97 such artificial diamonds are shown as seen under the microscope.

Although the pure diamond is colourless, diamonds of all possible colours, especially yellow, and from brown to black, occur in nature.

The latter, which have no value as gems, are used for technical purposes. The colours are due to impurities, especially organic substances.

As regards the mutual stability-relations of these different forms of carbon, we possess as yet no exact knowledge, for the transitions take place here with such excessive slowness that it is hardly possible to follow them experimentally. The following has been established with some degree of certainty.

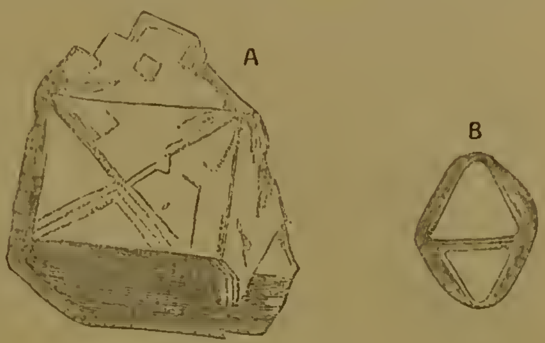


FIG. 97.

Amorphous carbon must be regarded as the least stable; it contains the greatest amount of energy. Graphite must, very probably, be regarded as the most stable at comparatively high temperatures. The reason of this is, especially, that at very high temperatures diamond passes into graphite. Accordingly, diamond would, with respect to stability, stand in the middle.

However, as is known, the relative stability of different forms of the same substance depends very much on the temperature, and it is, therefore, not admissible to directly draw conclusions as to the relations at ordinary temperatures from those existing at 3000°.

Compounds with Oxygen.—Carbon forms two oxides, one combining weight of carbon being able to unite with one or with two combining weights of oxygen. The second of these compounds is by far the more important.

Carbon dioxide, CO_2, is a gas with the normal weight 44; it is colourless, has a feeble but distinct taste and smell, and dissolves fairly readily in water. At room temperature, water absorbs about an equal volume of the gas. With changes of pressure and temperature, carbon dioxide shows appreciable deviations from the simple gas laws; by increase of pressure it can be readily liquefied. In the following table the vapour pressures of carbon dioxide are given; these are equal to the pressures which must just be exceeded in order that the gas may pass into a liquid.

Temperature.	Pressure.	Temperature.	Pressure.
− 80°	1·00 atm.	− 10°	26·76 atm.
− 70°	2·08 ,,	0°	35·40 ,,
− 60°	3·90 ,,	+ 10°	46·05 ,,
− 50°	6·80 ,,	+ 20°	58·84 ,,
− 40°	10·25 ,,	+ 30°	73·84 ,,
− 30°	15·15 ,,	+ 31°	75·56 ,,
− 20°	19·93 ,,		

As can be seen from this table, the pressure of liquefaction at 0°

is equal to 35 atm.; at − 80° the pressure of 1 atm. is sufficient, in order to liquefy the gas. The critical temperature is 31°; this is the limit up to which the conversion of the gas to a liquid can be effected by pressure.

The Critical Phenomena.—Since it was in the case of carbon dioxide that the critical phenomena were first discovered in their mutual connection, it will be appropriate to discuss them more fully at this point. This will be best done with the help of a diagram representing the relation of pressure and volume.

In Fig. 98, the volumes are measured to the right and the pressures upwards. For every temperature there will then be a line which will represent the corresponding values of pressure and volume. If, therefore, any definite temperature is taken, there will correspond to each pressure a definite volume, and *vice versa;* all the corresponding values of these will be represented by a connecting line, which is called an *isotherm*, because it is a line of constant temperature.

For liquids, the isotherms have the following form. If the pressure weighing on a liquid be changed, the volume changes in the opposite sense, but only to a very small amount, because the compressibility of liquids is very small. If, therefore, in the above mentioned diagram, we measure the volumes to the right and the pressures upwards, we obtain an almost perpendicular line, since almost identical volumes correspond to very different pressures, and the former, therefore, lie almost exactly under one another. On account of the slight increase of volume with diminishing pressure, the isotherm for liquids inclines slightly to the right, if we follow it from above downwards, that is, in the direction of smaller pressures. In Fig. 98, the line marked 13·1° shows on the left such a liquid-isotherm.

At a definite minimal pressure, vapour begins to be evolved from the liquid. If we now attempt to further lower the pressure by increasing the volume, we do not succeed, but more vapour is given off and the pressure remains unchanged, the temperature being supposed constant. A line representing constant pressure with changing volume is a horizontal line in our diagram. For the states consisting of liquid and vapour, the isotherm is, therefore, a horizontal line, *e.g.* the middle portion of the line 13·1° in Fig. 98. On continually increasing the volume, all the liquid finally evaporates, and only vapour is now present. So soon as this occurs, the pressure again diminishes as the volume increases, but to a much less extent than in the liquid state. The vapour formed follows approximately the law of Boyle, $pv =$ const., and the isotherm is represented by a portion of a line such as in Fig. 18, p. 76, or a hyperbola. This is the right end of the line 13·1° in Fig. 98.

If now we apply the same considerations to another isotherm at a higher temperature, we may, to begin with, repeat what has been said word for word. The difference which exists, consists in the fact that the volumes of the liquid, on account of the higher temperature, are rather greater than previously, under the same pressures; the liquid-isotherm, therefore, lies to the right of the previous one. Further, the vapour, on account of the higher temperature, appears at a greater pressure; the horizontal portion of the isotherm, therefore, starts higher up than previously. Finally, the liquid entirely evaporates at a smaller volume. For, even if on account of the higher temperature the vapour should have, at a given pressure, a smaller density, still the increase of the vapour pressure by which the volume is diminished, amounts to much more, and the total result is a considerable diminution of the volume of the vapour. The form for such an isotherm at a higher temperature is represented in Fig. 98 by the curve marked with 21·1°, in which the above mentioned differences from the lower isotherm for 13·1° can be seen.

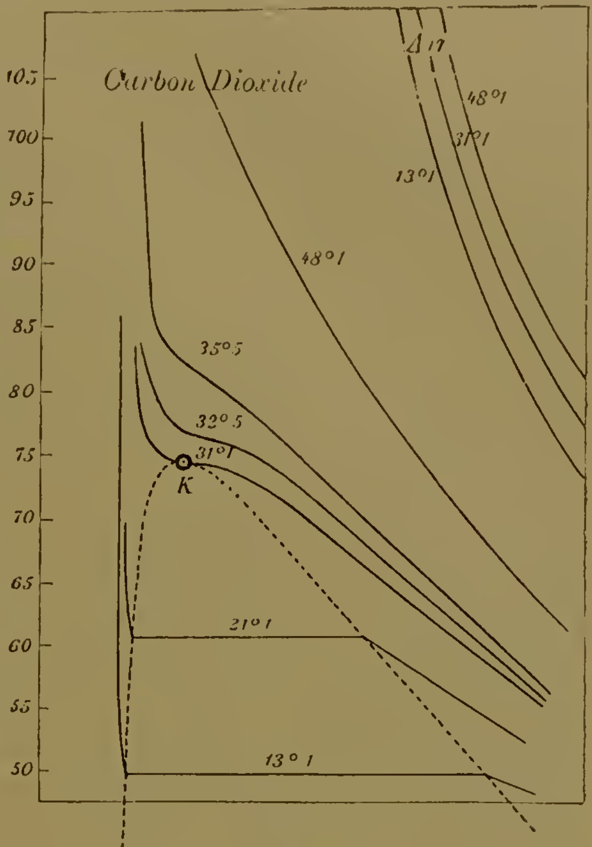


Fig. 98.

The higher, now, the temperature is taken, the nearer do the two ends of the horizontal straight lines come together, *i.e.* the less do the volumes or the densities of the liquid and of the vapour differ from one another. On the isotherm 31·1° the two finally come together in the point K.

The meaning of this is that in the point K, the densities of liquid and vapour have become equal, and since, apart from this, the composition and chemical nature are the same, the two states become completely identical. At this point, the critical point, therefore, the distinction between liquid and vapour disappears.

At still higher temperatures the isotherms, of which there are still some in the diagram, have no horizontal middle portion but are continuous. *Here, accordingly, the phenomena of liquefaction and evaporation are no longer possible, and all changes of state take place continuously.* At first the proximity of the critical point makes itself still evident in the flexures of the isotherms, as is clearly shown in the isotherms 32·5° and 35·5°; at 48·1°, however, these have also disappeared, and the isotherms no longer differ essentially from those of a gas. The corresponding isotherms for air are inserted to the right at the top of the diagram; these show that carbon dioxide, under the high pressures employed, deviate from the gas laws in such a way that the volumes are considerably smaller than in the case of a perfect gas.

The region enclosed by the curved, dotted line, in which the horizontals representing the states liquid plus vapour lie, can be called the region of *heterogeneous states*, since in it two phases are present. Everywhere else, there is only one phase present: at the left edge, liquid; at the right, vapour. The diagram shows that *above the critical point these two latter regions are continuously connected with one another.* In other words, it must be possible to convert a liquid into a vapour or a vapour into a liquid without the one ever being observed to separate from the other, or without liquid ever visibly passing into vapour, or *vice versa.*

To perform this, carbon dioxide is first compressed at a low temperature, so that it is completely converted into a *liquid.* One thus commences with a point which lies to the left of the region of heterogeneous states. If, now, the pressure is always maintained high enough so as to remain in this region, and the temperature be raised above 31·1°, we always remain to the left of the central field but reach a point higher than the point K. If the pressure is now diminished, while the temperature is maintained above the critical value, we pass to the right along one of the isotherms. On this isotherm the pressure can be diminished to any desired extent, and the temperature also can be allowed to fall; so long as one avoids coming into the heterogeneous region, the carbon dioxide is undoubtedly in the *gaseous* state, a fact of which one can convince oneself by reducing the pressure to that of the atmosphere and opening the vessel.

Similarly, just as along a path above the point K, a liquid can be converted continuously into a vapour or a gas without vapour ever making its appearance along with it, so it is possible to convert a gas continuously into a liquid without a separation of liquid ever becoming visible. For that purpose, it is only necessary to raise the temperature above the critical value, and the gas can then be compressed without its liquefying. Above the pressure corresponding to the point K, or the critical pressure, the temperature can be lowered below 31·1°. If the pressure be now diminished, it is found that the substance exists in the liquid state.

The critical point K is characterised by three magnitudes: the critical temperature, or the temperature of the isotherm in which liquid and vapour become identical; the critical pressure corresponding to this; and the critical volume or the critical density. The two latter are the values of the pressure and volume, or density, at the point K.

They are obtained from the diagram by reading off the corresponding distances on the axes of pressure and volume. Thus, the critical pressure of carbon dioxide is found to be about 75 atm. The critical volume has to be referred to some definite quantity of substance; for one mole, or 44 gm. carbon dioxide, it amounts to 112 cc.

Three such critical constants belong to every pure substance. Whereas the critical temperatures are to be found ranging from the lowest to the highest temperatures, the critical pressures move within fairly narrow limits, between 20 and 100 atmospheres, which they exceed only in quite exceptional cases. The critical volumes of one mole are also not very different; like the other critical constants, they increase with the molar weight of the respective substances, and vary from 10 to some hundred cubic centimetres.

Liquid Carbon Dioxide.—On account of the moderate pressure by which carbon dioxide can be liquefied, even at the ordinary temperature, this substance is now placed on the market in large quantities in the liquid form. For this purpose, the gas is pumped into iron cylinders (Fig. 37, p. 103), which are kept cool, and is thereby converted into the liquid state. The starting material, carbon dioxide gas, occurs abundantly in various localities. Especially in districts where volcanic activity, previous or existing, can be recognised, copious streams of carbon dioxide are frequently found escaping from fissures in the earth, and this gas is suitable for being directly liquefied. In Germany, such sources of carbon dioxide exist especially in the Eifel district.

If liquid carbon dioxide be allowed to stream out into the air, part of it immediately evaporates. So much heat is thereby withdrawn from the remainder that its temperature sinks below the point of solidification of carbon dioxide, and the latter solidifies in the form of a white snow. By allowing the liquid to stream into a bag of closely woven cloth, the "carbonic acid snow" can be filtered off, the solid remaining in the bag while the gaseous portion escapes through the fabric.

The solid dioxide is used chiefly for producing low temperatures. For this purpose it is mixed with ether, which still remains liquid at the temperature produced, and a paste is thus obtained whose temperature is $-80°$. In a space pumped as vacuous as possible, the temperature of this freezing mixture sinks, in consequence of the accelerated evaporation, to $-100°$.

Solution in Water.—In water, carbon dioxide dissolves in accordance with the law of Henry (p. 271). The aqueous solution has an acidulous taste and causes a prickling sensation. The refreshing taste of spring water is produced essentially by the presence of carbon dioxide, which is present in abundance in most natural waters. It passes into these from the soil, where it is being constantly developed in the slow combustion of the organic substances by the oxygen of the air. Since the saturation with this gas has taken place at a low temperature, such waters are generally supersaturated, and when they become warmer by standing in the air, the gas slowly forms bubbles on the walls of the vessels. This formation of bubbles in water containing carbon dioxide is regarded as a sign of a palatable drinking water. It of course gives no security against the presence of other substances of a harmful nature.

Water in which carbon dioxide is dissolved in somewhat larger amounts frequently occurs in nature, and is used, as aerated or mineral waters, for medicinal purposes or as a beverage. Large quantities of water artificially saturated with carbon dioxide under the pressure of from two to three atmospheres are prepared, and are used, with addition of various salts, for the same purposes.

Liquids containing carbon dioxide are also produced in the fermentation of solutions containing sugar. In this process the sugar decomposes into alcohol and carbon dioxide, and in certain liquids of this kind, *e.g.* beer and sparkling wine, the fermentation is conducted in such a way that the carbon dioxide does not escape, but remains dissolved, in larger or smaller amounts, in the liquid.

For the preparation of aerated liquids, the gas was formerly chiefly prepared from naturally occurring compounds, the carbonates, by means of acids. At the present time, liquid carbon dioxide is chiefly employed, being manufactured in large quantities and placed on the market at a very low price.

Carbonic Acid.—The solution of carbon dioxide reacts feebly acid to litmus, the colouring substance being rendered not bright red but only wine red. This, however, is essentially due to the small concentration obtained in aqueous solutions of the gas under ordinary pressure. If the amount dissolved is increased by using higher pressures, a solution is obtained which also gives the ordinary bright red colour with litmus.

In the aqueous solution, therefore, there is an acid present, and carbon dioxide is to be looked upon as the anhydride of this acid. The relations are the same as in the case of sulphurous acid; the formula of carbonic acid is H_2CO_3, and it decomposes with extreme readiness into water and the anhydride CO_2, carbon dioxide or carbonic acid anhydride.

Carbonic acid is a dibasic acid with very slightly developed acid properties. Like the dibasic acids in general, it forms two kinds of anions, the monovalent HCO_3' and the divalent CO_3''. Since even the process $H_2CO_3 = H^\cdot + HCO_3'$ takes place only to a very slight extent, the second stage of dissociation, $HCO_3' = H^\cdot + CO_3''$, is, for most purposes, inappreciably small. In aqueous solution, therefore, the monovalent ion HCO_3' is formed by preference, and to this some of the characteristic properties of the carbonates are due.

The *salts of carbonic acid*, or the *carbonates*, are mostly very difficultly soluble in water; only those of the alkali metals form an exception and are easily soluble. The latter react fairly strongly alkaline, since from the tendency of the ion CO_3'' to interact with water and pass into HCO_3' $(CO_3'' + H_2O = HCO_3' + OH')$, a certain amount of hydroxidion is produced, whereby the alkaline reaction is effected. On addition of acids, all carbonates evolve carbon dioxide. Carbonic acid is first formed, but this can exist in aqueous solution only to a small extent and mostly decomposes into the anhydride and water: $H_2CO_3 = CO_2 + H_2O$. Since carbonic acid is, as has just been mentioned, a very feeble acid, this reaction is brought about also by other weak acids, and the power of expelling carbon dioxide from carbonates can almost be considered as a characteristic of the acids.

The "Circulation" of Carbon.—In nature, carbonic acid and the carbonates occur in very large quantities. The air always contains carbon dioxide, the amount of which varies somewhat. In places where there is no special source of the gas present, the amount is about $\frac{1}{2000}$th of the volume of the air. This amount is increased by organic respiration and combustion processes of all kinds; added to this, there are also considerable amounts of carbon dioxide derived from volcanic action.

All organisms make up for the waste necessary for their vital activity by the consumption of chemical energy, which, for the greatest part, is the energy of the oxidation of carbon. Whereas animals and those plants which do not contain chlorophyll can carry out the oxidation only of already existing carbon compounds, and live from these, the green plants can also carry out the opposite process; they can decompose carbon dioxide into carbon (or compounds of carbon) and free oxygen. For this a considerable expenditure of energy is necessary, and this the green plants derive from the radiant energy of sunlight. They thereby store up not only the supply of energy which they require for their own life, but they also yield the supply of energy which is used by all the other organisms and which these take up in the form of food. By the oxidation of this carbonaceous food, first of all the herbivorous and then indirectly through the medium of these, the carnivorous animals obtain their vital energy.

By means of the oxidation in respiration, the carbon again returns to the air as carbon dioxide, and a "circulation of carbon" is produced by which the mutual preservation of the vegetable and animal kingdoms appears to be lastingly assured. However, for this end, it is not the conservation of the *carbon* that is the real problem here; the rôle of carbon is only to effect the transport of *energy*, which is the essential thing. In fact, certain organisms are known, *e.g.* the sulphur bacteria, which obtain their vital energy not from the oxidation of carbon compounds but by quite different chemical reactions. There are, therefore, organisms which do not require any carbon for their nourishment; no organism, however, is conceivable which would not require to have free energy at its disposal in order to exhibit any kind of vital activity.

So far, now, as our knowledge extends, no such cycle exists for energy. Here it is a case of a current flowing in one direction, which pours out from the sun on to the earth, where it is partly used up and partly stored up by the plants. The supplies stored up by the plants are for the greatest part further used up by the other organisms, but a smaller part is preserved as fossil combustible material and serves in later times as the most important source of energy in the industrial life of man. That the free energy which is derived from the sun and which in this way is finally used up, will by any process be again made disposable, we have no sign; on the contrary, from the experience which has been gained with the terrestrial processes, it is to be assumed as probable that such a reverse process, corresponding to the spontaneous flow of a stream uphill, is not possible (p. 132). It is, therefore, of essential interest for the permanent maintenance of life that as large a portion as possible of the radiant energy of the sun should be brought into the storable form of chemical energy, and that, therefore, as large a part as possible of the earth's surface be covered with green plants. As is well known, great improvements in this respect are still possible.

If one considers that, as already mentioned, the amounts of energy used in the industries are also derived for the most part from the chemical energy of carbon, namely, in so far as they are obtained by the combustion of coal or other fossil fuel, we see that this element is, in fact, along with oxygen, the most important carrier of chemical energy, indeed, of any energy whatever. It would be incorrect to designate carbon alone as the carrier. The quantities of energy in question become free only by combustion, *i.e.* when the carbon combines with oxygen, and we must not assert that the energy was contained solely in the one or other element. In other words, we are dealing with the energy equation

$$C + O_2 = CO_2 + 406\ kj,$$

and for this, each member is of equal importance. Only, the carbon readily appears to be the sole carrier of the energy because the oxygen is generally accessible in the air and does not, therefore, require to be specially prepared and bought. If the plants did not separate the oxygen in the gaseous form but as a solid compound rich in oxygen, the latter would be just as necessary for the conservation of life and the heating of steam engines, as the solid carbon compounds; it, also, would be consumed by animals, and would also be collected by man and placed on the market.

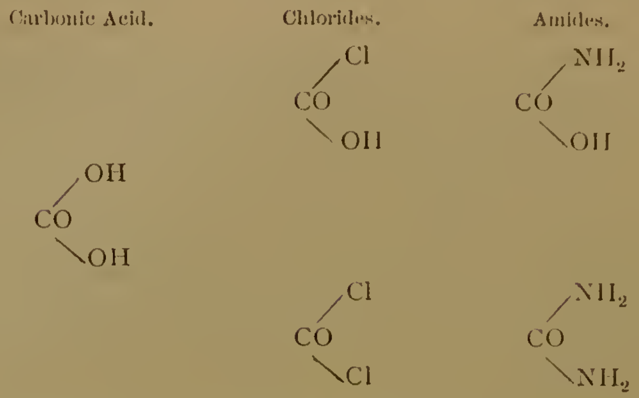
The Combining Weight of Carbon has been determined by combustion to carbon dioxide. The latter can be completely retained by a concentrated solution of caustic potash or soda and weighed. If, therefore, the carbon is weighed, and also the potash apparatus before and after the experiment, we can ascertain how much carbon dioxide has been formed by the combustion, and, by difference, how much oxygen has combined with the carbon. In this way, pure amorphous charcoal as well as graphite and diamond have been investigated; with all three, exactly the same ratio has been obtained, so that the different quantities of energy present in the different forms of carbon exert no influence on the combining weight. The uniform result of the determinations was that exactly 12·00 of carbon unite with two combining weights (=32) of oxygen, so that we have to put C = 12·00.

Detection of Carbonic Acid.—Although carbon dioxide on being dissolved in water yields only very feebly acid solutions, it readily forms salts with dissolved bases; it is, therefore, rapidly and completely absorbed by solutions of these. This behaviour is made use of for the detection and quantitative determination of carbon dioxide (*e.g.* in the air), and those bases more especially are employed which form insoluble carbonates. Most frequently there is used a solution of lime or calcium hydroxide, $Ca(OH)_2$, which forms with the dibasic carbonic acid the salt $CaCO_3$, or calcium carbonate. This is precipitated from the solution in the form of a white powder, and by means of it small quantities of carbonic acid can be detected.

The formation of this white precipitate is sufficient for the qualitative proof of the presence of carbonic acid. If a quantitative determination has to be made, a measured volume of the lime solution (lime water), the strength of which has been determined by titration with an acid (p. 186), is taken, and after the reaction has occurred the precipitate is allowed to settle, and the amount of lime remaining is determined in a measured portion of the clear liquid; the difference is a measure of the carbon dioxide absorbed.

Derivatives of Carbonic Acid.—Although carbonic acid itself is not known, there exist not only a large number of salts which are derived from it, but also compounds formed by the replacement of its hydroxyls; more especially, the chlorides and amides of carbonic acid are known, some of which are of very great importance.

If carbonic acid be written as a hydroxyl compound, there are possible, on account of the presence of two hydroxyls, two chlorides and two amides, exactly as we found in the case of sulphuric acid (p. 302). Represented schematically, we have the following compounds:—



All these substances are known, some, however, only in the form of compounds.

The *carbon oxychloride*, $COCl_2$, or *carbonyl chloride* (the residue CO is called carbonyl), is produced directly from carbon monoxide (p. 394) and chlorine, by mixing these two gases in equal proportions and exposing to sunlight. Here, as in many other cases, the action of chlorine is very markedly accelerated by the influence of light. To this is also due the name "phosgene gas" for carbonyl chloride. Since, however, the compound is also formed without the aid of light, we are not dealing here with the communication of a necessary energy, as in the case of the reduction of carbon dioxide in the green plants (p. 389), but merely with a case of acceleration; the light acts catalytically.

In defect of sunlight, charcoal can also be used as catalyser: combination likewise takes place, especially on passing the gaseous mixture over animal charcoal.

The reaction occurs in accordance with the equation $CO + Cl_2 = COCl_2$. That is to say, one volume of each of the two components unites to form one volume of the compound.

Carbon oxychloride is a colourless gas with a suffocating odour, and can be readily liquefied by means of a freezing mixture; it boils, under atmospheric pressure, at + 8°.

Carbon oxychloride behaves chemically as a true acid chloride. It is decomposed by water, forming carbonic acid and hydrochloric acid, and by ammonia with formation of ammonium chloride and the amide of carbonic acid (*vide infra*).

The first chloride of carbonic acid, or chlorocarbonic acid, $ClCOOH$, is usually called chlorformic acid, since the corresponding hydrogen compound, the monobasic acid $HCOOH$, is called formic acid. It is not known in the free state, but only as a constituent of more complex compounds; these belong to organic chemistry, and will, therefore, not be treated in detail here.

Amides of Carbonic Acid.—As has already been mentioned, the amide of carbonic acid is formed by the action of ammonia on carbonyl chloride, in accordance with the general reaction as represented by the equation $COCl_2 + 4NH_3 = CO(NH_2)_2 + 2NH_4Cl$. These two substances can be separated by treatment with alcohol, in which the amide, but not the ammonium chloride, is soluble, and the carbonic acid amide, or carbamide, is obtained as white crystals which are soluble in water, and have a cooling and somewhat bitter taste. They have no saline character, and their aqueous solution does not conduct the electric current.

The same substance is formed in the bodies of the mammals, especially the carnivora, as the final product of the metabolism of the nitrogen which is contained in the food and consumed in vital activity, and leaves the organism dissolved in the watery excretion, the urine. From the urine of the carnivora, after being concentrated, it mostly crystallises directly; from that of the omnivora, especially of man, it cannot be obtained in this simple way, since its crystallisation is hindered by the presence of other substances. To the concentrated liquid, strong nitric acid is added; a difficultly soluble compound is then formed which crystallises out, and from which the substance can be easily obtained by converting the nitric acid into a salt by any base. From its occurrence in urine, the compound is usually called *urea*.

As amide of carbonic acid, urea has the property of passing, by combination with water, into the ammonium salt of carbonic acid: $CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3$. At the ordinary temperature this change is exceedingly slow; at 100°, however, appreciable amounts of ammonium carbonate are formed in an aqueous solution of urea, and if acid is added, the transformation proceeds still more quickly, the carbonic acid being evolved, and the corresponding ammonium salt remaining in solution. Strong bases have a similar action. In putrefying urine ferments are present which have been formed by the schizomycetes which vegetate in the urine, and these have the power of accelerating this absorption of water by urea, even in neutral solution. Sometimes such ferments are present in the bladder of the living organism; the ammonium carbonate then formed has a corrosive action on the organism, and can cause very severe illness.

On account of its occurrence in the animal organism, urea was classed with the organic compounds before its simple relation to carbonic acid had been discovered. Since the organic compounds were formerly regarded as being produced under the influence of a special force, the vital force, the actions of which, it was assumed, could not be effected outside the organism, a great sensation was caused when, in 1828, F. Wöhler discovered a method of preparing urea artificially. This consists in the transformation which the ammonium salt of cyanic acid experiences in aqueous solution, and will be described somewhat later.

This first "synthesis" of an organic compound was followed later by innumerable others, and although by no means all the compounds which occur in animals and plants have as yet been artificially prepared, still in the work which has been directed towards this end, no circumstance has been encountered which makes it improbable that, on more thorough investigation, it will be possible to artificially prepare all the constituents of the organisms.

The other amide of carbonic acid has the formula $\mathrm{CO}\begin{matrix}\mathrm{NH_2}\\ \mathrm{OH}\end{matrix}$; it is, therefore, an acid, and is called *carbamic acid.*

Carbamic acid itself is not known. Its salts are produced when ammonia and carbon dioxide come together in presence of bases. Thus, the calcium salt is obtained by adding ammonia to calcium hydroxide and passing carbon dioxide into the mixture. Since calcium carbamate, $Ca(OCONH_2)_2$, is soluble in water, while calcium carbonate is not, the formation of a soluble calcium salt in the above circumstances is a proof of the formation of the new salt.

The ammonium salt of carbamic acid is formed as a white crystalline mass on bringing ammonia and carbon dioxide together. This can be carried out directly with the two gases, or, more conveniently, the gases are passed into anhydrous alcohol, in which the ammonium carbamate soon separates out as an insoluble solid.

In accordance with the formula of the acid, the composition of the salt is given by the formula NH_4OCONH_2. If we write the summed formula we obtain $CO_2N_2H_6$, *i.e.* the sum of one mole carbon dioxide and two moles ammonia. This is the explanation why the salt can be formed directly by the union of the two gases.

By themselves, the carbamates, even in aqueous solution, are fairly stable, especially when the solution has an alkaline reaction. If, however, the liquid is acidified, an ammonium salt is formed and carbon dioxide is liberated. This reaction is represented by the equation $HOCONH_2 = NH_3 + CO_2$, which shows that carbamic acid can pass directly into ammonia and carbon dioxide.

Carbon Monoxide.—When coal is burned in a restricted supply of air, a gas is formed which can burn in the air with a characteristic blue flame, forming carbon dioxide. This phenomenon is easily seen in a coal fire. When most of the hydrogen compounds present have been burned, and the coal has become quite incandescent, the coal lying at the foot of the grate which comes into contact with the entering air, burns, it is true, to carbon dioxide, but this gas, on passing through the upper layer of glowing coal is, in accordance with the equation $CO_2 + C = 2CO$, reduced to the compound CO, which represents the above combustible gas. At the top of the glowing layer, where abundance of air can again find access, the gas burns to dioxide with the above-mentioned blue flame.

This compound, therefore, can be obtained by passing carbon dioxide over strongly heated charcoal. Since in this process much heat is taken up, this must be communicated from without, *i.e.* the tube must be strongly heated. If the issuing gas is passed through a solution of caustic soda, the carbon dioxide which remains undecomposed is absorbed, and the residue is pure carbon monoxide.

Carbon monoxide is a colourless gas with the molar weight 28; it must, therefore, have the formula CO. The density is equal to that of nitrogen, and most of the physical properties of the two equally dense gases also show close agreement. Thus, the critical magnitudes are :—

	Carbon monoxide.	Nitrogen.
Critical temperature	−140°	−146°
Critical pressure	36 atm.	35 atm.
Critical molecular volume . .	—	103 cc.

The solubility of the two gases in water is also equally small.

Of the special properties of carbon monoxide, its poisonousness should be mentioned, which, in certain circumstances, makes it a very dangerous substance. This depends on the fact that the gas can combine to form a very stable compound with hæmoglobin, the colouring matter of the red blood corpuscles. Now, hæmoglobin has the function of taking up the oxygen inspired into the lungs and of conveying it through the blood canals to the parts of the body where, by its oxidising action on the different tissues and their constituents, it maintains vital activity. But if the hæmoglobin combines with carbon monoxide, it loses the power of taking up oxygen, and precisely the same effects supervene as on suffocation.

Such cases of carbon monoxide poisoning easily occur when coal is burned in a stove which has an insufficient outlet, or if this outlet be closed. Every year such cases of poisoning occur through closing the stove register too soon. Carbon monoxide poisoning may also be occasioned by coal gas, which, on an average, contains 0·1 of its volume of carbon monoxide. Certain kinds of gas which are obtained by the action of steam on heated charcoal (water gas) contain much more carbon monoxide, and their use in daily life is, therefore, not without objection.

* The presence of carbon monoxide can be detected by the fact that it is so readily absorbed by hæmoglobin. If the gas to be investigated is passed into a solution of the colouring matter of the blood, the presence of carbon monoxide is shown by the appearance of two characteristic bands in the absorption spectrum of the colouring matter. These, it is true, appear similar to those produced by oxygen, but they can be distinguished from the latter by the fact that on addition of reducing agents (*e.g.* sodium sulphide) they do not disappear, whereas the oxygen bands do.

With oxygen, carbon monoxide burns to dioxide in accordance with the equation $2CO + O_2 = 2CO_2$. Two volumes, therefore, of the monoxide unite with one volume of oxygen to yield two volumes of carbon dioxide, and in this respect the relations correspond exactly to those of detonating gas obtained from hydrogen and oxygen. With oxygen or air, carbon monoxide also yields a detonating gas or explosive mixture, which, however, burns much less violently than the former.

This is not in any way due to a smaller development of heat, the heat of combustion being in both cases almost exactly the same, for it amounts to 284 *kj* for one mole of carbon monoxide, and 286 *kj* for one mole hydrogen. The cause is that the *velocity* with which the process of combustion is propagated in the explosive mixture, is much smaller in the case of the carbon monoxide and oxygen than of the hydrogen and oxygen mixture.

This velocity is greatly increased by the presence of a trace of water vapour. In the case of the carbon monoxide mixture which has been carefully dried with phosphorus pentoxide, the velocity is so small that it is not possible to bring about ignition by means of an electric spark; a mixture of perfectly dry carbon monoxide and oxygen appears to be incombustible in such a way. If, however, the mixture is heated from without, combination takes place.

* The same behaviour is evidenced by the fact that a jet of carbon monoxide burns in moist air with the well-known blue flame, but is extinguished when it is brought into dry oxygen, whereas it continues to burn in the moist gas.

* All these are catalytic actions. The assumption occasionally expressed that intermediate products are formed with the water, has not been proved; it may be right, but the mere assumption contributes nothing to the explanation of the phenomenon itself.

Water Gas.—The great advantages possessed by gaseous fuel with respect to completeness of combustion and power of regulating the flame, have given rise to many experiments to prepare such a gas, with as small a loss as possible, from the solid material, coal or lignite. A very promising reaction was found in the action of water vapour on charcoal, corresponding, according to circumstances, to one or other of the equations

$$C + H_2O = CO + H_2$$
$$C + 2H_2O = 2H_2 + CO_2.$$

In the former case, charcoal and water vapour are converted into carbon monoxide and hydrogen, in the latter, into carbon dioxide and hydrogen. Of the two reactions, the former predominates at high temperatures, while the second is favoured by a lowering of the temperature.

Neither of the two reactions can take place spontaneously, for each is accompanied by an absorption of heat, amounting in the first case to

133 *kj*, and in the second to 91 *kj*. The communication of the necessary energy in some form must, therefore, be provided for. One method consists in raising the coal to a high temperature by combustion with the help of an air-blast, and then passing in steam; when the temperature has again sunk so low that the reaction would cease, air is again injected, and the processes are repeated alternately. In these operations, care must be taken, by reversing the conducting tubes, that the mixture of carbon dioxide and nitrogen formed in the heating process does not mix with the combustible gas formed in another period of the process.

The second method consists in mixing the steam with as much air as is necessary to maintain the temperature. The process is in this way a continuous one, and therefore much simpler, but the gas produced has the disadvantage that it contains a fairly large amount of carbon dioxide and nitrogen mixed with it, and therefore does not allow of such high temperatures being attained as the pure "water gas."

On account of the very poisonous nature of carbon monoxide, it will always be better to aim at producing a gas which contains as little carbon monoxide as possible and a correspondingly larger amount of hydrogen. This is the same as saying that the operations should be carried out at as low a temperature as possible.

Formic Acid.—Carbon monoxide can be regarded as the anhydride of an acid which is called *formic acid* ($CO + H_2O = HCOOH$), because it was first observed in the acid liquid which ants squirt out for defensive purposes. Still, no appreciable amount of formic acid is formed when carbon monoxide and water are brought together. The sodium salt, or sodium formate, however, is obtained when carbon monoxide is passed over gently heated caustic soda. The reaction is $CO + NaOH = HCOONa$.

As is seen from the formula of the sodium salt, formic acid is a monobasic acid in spite of the fact that it contains two combining weights of hydrogen. One of these is not capable of being replaced by metals, the other, however, can be so very well. Formic acid cannot even be called an acid of medium strength, although it approaches very near to one.

Free formic acid can be easily obtained by the distillation of the sodium salt with sulphuric acid. It is rather difficult to remove the last traces of water from it, since it readily decomposes again into water and carbon monoxide. It is best effected by allowing the fairly concentrated acid to partially solidify; an anhydrous acid then crystallises out and a more watery mother liquor remains. Pure formic acid melts at 8·6°; at the ordinary temperature it is a colourless liquid with corrosive smell and action, which dissolves in water in all proportions and reacts strongly acid. With bases or metals, it forms salts which are mostly easily soluble in water; by oxidising agents, it is readily oxidised to carbon dioxide: $HCOOH + O = CO_2 + H_2O$. It acts, therefore, with respect to some substances, as a reducing agent, and it precipitates, more especially, the noble metals such as gold and platinum, but also silver and mercury, from their salts.

Formic acid is usually classed with the organic acids because it is the first member of a large series of similar acids which differ from it in the fact that the non-ionisable hydrogen is replaced by the atomic group C_nH_{2n+1} (n being a whole number); in the simplest case, therefore, by CH_3. The acid which is formed from formic acid by the introduction of CH_3 in place of hydrogen, is called *acetic acid;* it has the composition $CH_3COOH = HC_2O_2H_3$, and is monobasic like formic acid. Since acetic acid is readily formed from organic substances, it is one of the longest known acids, and in most languages it has given the name to the group of the acids.

Acetic acid has similar properties to formic acid; it does not, however, exhibit the reducing actions of the latter, but is exceedingly stable towards oxidising agents. It is a colourless liquid which solidifies (when supercooling is avoided) at 17·5°, and which, on account of the ice-like appearance of the crystals, is called glacial acetic acid. It mixes with water in all proportions, yielding solutions of an acid taste. A solution containing about 3 per cent of acetic acid is used for household purposes under the name vinegar. In the laboratory also, acetic acid is often used in cases where it is necessary to have an acid which is much weaker than the mineral acids, hydrochloric or sulphuric acid, but which has nevertheless a distinct acid character and does not readily yield to other chemical attacks.

Hydrogen Compounds of Carbon.—The number of compounds which carbon forms with hydrogen is exceedingly great. The treatment of these belongs to organic chemistry, and only a few of the most important of the compounds of this group will be mentioned here, and their relations to the other simple carbon compounds discussed.

The simplest of all the substances of this group is the compound CH_4, which, from its occurrence, goes by the name of marsh-gas or fire-damp; its systematic name is *methane.* It is a component of the gases which are evolved from decaying vegetation at the bottom of stagnant waters. The gas is also frequently found in coal mines; it generally occurs shut up in cavities under some pressure, and escapes when these are opened in the mining. The name methane is derived from the relation which the gas bears to methyl alcohol (*vide infra*) or wood spirit.

Methane is a colourless and odourless gas, having the molar weight 16; it is slightly absorbed by water, and, in its properties, greatly resembles the simple gases nitrogen and hydrogen. It burns with a feebly luminous flame, and forms an explosive mixture when mixed with oxygen or air. Such mixtures are readily formed in coal mines, and do great damage when by any means they are ignited.

From the equation of combustion, $CH_4 + 2O_2 = CO_2 + 2H_2O$, it is seen that one volume of methane requires two volumes of oxygen, and therefore ten volumes of air, for its combustion. In order that a mixture shall remain explosive it must contain not less than six and not more than fourteen volumes of air to one volume of methane. Mixtures lying outside these limits can, indeed, be caused to react by heating, but they no longer explode, because the flame is extinguished even when ignition has been effected at one point.

The cause of this is, that in a mixture consisting of oxygen and a combustible gas, the ignition is propagated with very different velocities, depending greatly on the nature of the gas and the ratio in which they are mixed. That ignition is propagated at all, is due to heat being developed by the combustion. If this is sufficient to raise the temperature of the adjacent unburnt gas so high that its temperature of rapid combustion is reached, the process is continued from point to point, and rapid, explosive combination is the result. If, however, through the addition of a foreign gas or excess of a gas, the temperature is so far lowered that the heat developed in unit of time is no longer sufficient to cover the losses due to cooling at the walls of the vessel, radiation, etc., then the temperature must fall, the velocity diminishes, the temperature falls still more, and the reaction stops. It must be possible, therefore, to reduce every explosive gas mixture to the limits of combustibility, and beyond them. This is, as a matter of fact, the case. But the influence of different gases depends not only on their capacity for heat, as might be supposed from what has been said, but also on their specific nature. This is explained by the fact that the gases added act not only on the temperature but also on the velocity of reaction. Since explosive combustion is influenced by the one as well as by the other magnitude, no one of them can alone determine the limit of combustibility.

Derivatives of Methane.—From methane, numerous compounds can be derived which are formed from it by *substitution*. In other words, they are compounds in which one or more hydrogens of methane are replaced by other elements or groups of elements. This kind of mutual relationship is very general in the case of the carbon compounds or the organic compounds, and a complete system of all organic substances can be built up by imagining them to be formed from one another by substitution.

The processes here considered must be carefully distinguished from the process of salt formation, in which hydrogen is also substituted. Whereas in the case of the acids, by no means all the hydrogen can be replaced, in the case of organic compounds, all the hydrogen can be substituted. Further, whereas the acid hydrogen can be replaced only by metals or metal-like groups, the hydrogen of organic compounds can be replaced by the most different elements or groups. Finally, the compounds which are formed in the case of the organic substances are not salts, but undissociable or indifferent compounds. It is, of course, not excluded that organic substances may also yield acids, bases, and salts, but the formation and transformation of these follow the same laws as in inorganic chemistry. With the organic compounds, both kinds of processes, salt formation and substitution, may occur, correspondingly different substances being produced.

Thus, for example, the following compounds are successively obtained by the action of chlorine on methane (under the influence of sunlight):—

Methyl chloride	CH_3Cl
Methylene chloride	CH_2Cl_2
Chloroform	$CHCl_3$
Tetrachlormethane	CCl_4

All these substances are formed from methane, the hydrogen being replaced step by step by chlorine. Further, all are indifferent or non-saline substances. Their properties change gradually with the increase in the amount of chlorine, as is shown in the following table:—

	Density.	Boiling point.
Methyl chloride . . .	0·9523	−23·7°
Methylene chloride . .	1·3778	+41·6°
Chloroform	1·5264	61·2°
Tetrachlormethane . .	1·6320	76·7°

All these substances are only slightly soluble in water. The solutions do not exhibit any of the reactions of chloridion, *i.e.* on addition of silver nitrate they remain clear. Also, neither the solutions nor the pure substances possess the property of conducting the electric current.

The derivatives of methane containing bromine or iodine in place of hydrogen, are perfectly similar; their properties also undergo a gradual change with increase in the amount of halogen. On the other hand, if the corresponding chlorine, bromine, and iodine compounds are arranged in a series, a similar gradation of properties is observed. This is shown, for the densities, in the following table:—

	Chlorine.	Bromine.	Iodine.
Simple substitution . .	0·952	1·664	2·199
Double ,, . .	1·378	2·084	3·342
Triple ,, . .	1·526	2·900	4·008
Quadruple ,, . .	1·632	–	4·32

Radicles.—Considering the compounds just described, CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4, we can formally regard the latter as chlorides of the groups CH_3, CH_2, CH, and C. Of these, the first is combined with one, the second with two, the third with three, and the fourth with four combining weights of chlorine. Just as we called a metal which can combine with two combining weights of chlorine, divalent, so we may call the group CH_2 divalent, and CH trivalent; in this sense, carbon is tetravalent.

It is a remarkable fact that hydrogen and the halogens do not form any other compounds with carbon, containing only one combining weight of this element, than the ones mentioned. In other words, in all these compounds carbon is tetravalent, for the number of the combining weights of hydrogen and the halogens together, is always equal to four.

On the other hand, the group CH_3 can be regarded as monovalent because it can combine with still one combining weight of hydrogen or halogen; alone, it is incapable of existing. Likewise, the group CH_2 is divalent, and so on.

The monovalent group CH_3 is called *methyl*, the divalent CH_2 *methylene*, the trivalent CH *methenyl*.

Of these groups or radicles, the first is the most important, for it forms by far the most derivatives. Such compounds are formed not only by the replacement of hydrogen by other elements, such as the halogens, but, instead of elements, monovalent *radicles*, such as hydroxyl or amidogen, may replace hydrogen and give rise to corresponding compounds. The number of such radicles is very great, for every existing compound can, by the loss of one combining weight of hydrogen or another element, pass into a monovalent radicle.

Methyl Alcohol.—Of these compounds, one of the most important is that with hydroxyl, CH_3OH, which is called *methyl alcohol*. Formerly, the name alcohol was used to designate only spirit of wine, the volatile constituent of intoxicating beverages. It afterwards became a class name, and the hydroxyl compounds of the hydrocarbon radicles generally are called by the name alcohol.

Methyl alcohol is formed, along with many other volatile substances, by the dry distillation, *i.e.* by the heating, of wood. It is separated from the mixture by fractional distillation, and in the pure state is a colourless liquid with a feeble odour and having the density 0·796. It is combustible and dissolves in water in all proportions. Its boiling point is 66°.

Methyl alcohol is a type of the *alcohols*. These are indifferent liquids, reacting neither acid nor alkaline with vegetable colours, whose aqueous solutions do not appreciably conduct the electric current, and which are therefore not dissociated into ions. The alcohols can be mixed with acids without immediate combination taking place. If the two substances, however, remain mixed for a lengthened period, interaction slowly occurs, the course of which is quite similar to that of salt formation. Thus, from methyl alcohol and hydrochloric acid, methyl chloride (p. 400) and water are formed, and the corresponding equation of reaction, $CH_3(OH) + HCl = CH_3Cl + H_2O$, has an appearance quite similar to that of a salt formation, the methyl, CH_3, playing the part of a cation.

However, the product of the action, the methyl chloride, is no salt in the ordinary sense. As is seen from the statement of its properties given on p. 400, it is, at the ordinary temperature, a gas which is converted into a colourless liquid only at – 23·7°. Its aqueous solution does not conduct the electric current at all, and on the addition of silver solution, no precipitate of silver chloride is formed, so that no demonstrable amount of chloridion is present.

If, however, the silver solution is left very long in contact with methyl chloride, silver chloride begins to slowly separate out. One is, therefore, led to suppose that chloridion is indeed present in the aqueous solution, but in exceedingly slight amount. By the long continued action of the silver solution the amount of chloridion is finally so far increased that silver chloride can be precipitated.

In fact, the most appropriate view of this kind of compound is that besides the outward similarity between the alcohols and the bases, and between their acid compounds and the salts, there exists an inner resemblance which is masked by the following circumstances. First, the dissociation of these substances into ions is so exceedingly small that it cannot be detected by the ordinary means. Secondly, the processes of dissociation into and recombination of the ions takes place disproportionately slower in the case of these substances (chiefly just by reason of the extraordinarily small concentration of their ions) than in the case of the typical bases and salts. It is suitable, therefore, not only to retain the name alcohol for the hydroxyl compounds, but also to call their acid derivatives not salts, but to introduce a special name for them. They are called *esters*. Methyl chloride is, therefore, the hydrochloric acid ester of methyl alcohol.

The Radicle Methyl and Homologous Series.—From methane, CH_4, which is a "saturated" compound, there is formed, by loss of hydrogen, a monovalent radicle which has the composition CH_3, and is called methyl. It does not exist alone any more than hydroxyl does; but as a constituent in organic compounds it plays a very important part.

This follows from the fact, discovered empirically, that those compounds in organic chemistry which may be regarded as being formed by the replacement of hydrogen by methyl, possess a very great resemblance to the parent compound. An example of this we have already met with in the case of formic and acetic acids. If we compare the two formulæ HCOOH and CH_3COOH, which represent these two acids, we see that, as a matter of fact, acetic acid can be derived from formic acid by imagining the first hydrogen of its formula replaced by methyl.

Such a method of derivation can be employed in the case of all organic compounds containing hydrogen. This can, in the first instance, be done for methane itself, and, in this way, there is obtained from methane CH_4 the compound $CH_3 . CH_3$, which is called ethane. In this compound, the same change can be carried out, and we obtain propane, $CH_3 . CH_2 . CH_3$. Evidently, there is no theoretical limit to this substitution, and, indeed, hydrocarbons of this kind are known up to C_{40} and over. *Petroleum* consists of hydrocarbons of this class.

On writing the summed formulæ of these hydrocarbons, we obtain the series CH_4, C_2H_6, C_3H_8, C_4H_{10}, and so on. Each successive hydrocarbon differs from the previous one by CH_2, one hydrogen being eliminated each time and CH_3 introduced instead. Such a series of similar compounds which can be derived from one another by the substitution of methyl for hydrogen, is called an *homologous series.*

Besides the homologous series of the hydrocarbons, there is one of the alcohols, the acids, the chlorides, etc.

Of the homologues of the above mentioned substances, we may mention *ethyl alcohol*, homologous to methyl alcohol, which is known under the name of spirit of wine, alcohol, or spirit. It has the composition CH_3CH_2OH or C_2H_6O, and can be derived from methyl alcohol by imagining one combining weight of hydrogen replaced by methyl.

Ethyl alcohol is prepared in very large quantities by the fermentation of sugar and substances containing sugar. These have the composition $C_6H_{12}O_6$, and decompose, under the influence of a catalytic agent which is secreted by various organisms, especially by yeast, into alcohol and carbon dioxide, according to the equation $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$. From the mixture produced, the ethyl alcohol is separated in the pure state by distillation. It boils at 80°.

Ethyl alcohol is a colourless liquid with a feeble smell and burning taste. For the organism it is, when concentrated, an acute, when diluted, a slow poison. The phenomena of incipient poisoning become first of all evident with respect to the brain, and, as alcoholic intoxication, are unfortunately too well known.

Alcohol is of very wide application in the arts. Apart from its occasional use as a clean fuel, easy to regulate, it is employed as a solvent for many substances, and as the starting-point for innumerable chemical preparations. It dissolves in water in all proportions, rise of temperature and diminution of volume thereby occurring. The density of the alcohol and water mixtures is used as an analytical aid in determining the amount in solution, and a large number of very exact determinations of this have been made. The following table gives a clear summary of the relations at 15°:—

Percentage amount of alcohol by weight.	Density.
0	0·9914
10	0·9755
20	0·9634
30	0·9495
40	0·9317

Percentage amount of alcohol by weight.	Density.
50	0·9108
60	0·8884
70	0·8652
80	0·8412
90	0·8160
100	0·7874

Ether.—In accordance with the majority of its reactions, alcoho must be regarded as the hydroxyl compound of the radicle ethyl, C_2H_5 If we recollect that hydroxyl is derived from water by the loss of on combining weight of hydrogen, it follows that alcohol can also b regarded as a derivative of water, one combining weight of hydroge being replaced by ethyl. From this the question at once arises, if th second combining weight of hydrogen in water cannot also be replace by ethyl or similar radicles. In the case of ethyl, a compoun $O(C_2H_5)_2$ would be formed.

Such a compound has long been known; it is called *ether*. Sinc similar substances can also be derived from methyl and the othe radicles, there exists a whole class of ethers of different composition which one distinguishes by stating the radicles contained in them Ordinary ether, $O(C_2H_5)_2$, is therefore called, by its scientific name *ethyl ether*.

Ether is obtained by distilling alcohol with concentrated sulphuri acid. If the summed formulæ of the two substances are compared, the formula of alcohol being doubled, viz., $2C_2H_6O$ or $C_4H_{12}O_2$ and $C_4H_{10}O$ it is seen that ether contains the elements of water less than tw combining weights of alcohol. Ether can, therefore, be regarded a an anhydride of alcohol, and the action of the sulphuric acid on alcoho in the formation of ether can be looked upon as a withdrawing o water. In reality, the process is rather more complex, but into that we cannot enter here.

Ether is a colourless liquid whose boiling point lies as low as 34·6 and has an easily recognisable, sweetish smell. It is combustible, and on account of its high vapour pressure, it rapidly evaporates in the open air with great lowering of temperature. The mixture of ether vapour and air is explosive. Ether has a narcotic action on the human organism, and is therefore used in surgical operations to produce unconsciousness, and therefore painlessness. If finely divided ether is sprayed on a part of the body, the latter becomes considerably cooled by the cold of evaporation, and in this way *local* numbness can be produced.

Ether is a solvent for many substances, *e.g.* iodine and bromine, as well as oils and fats. On this, likewise, many applications of ether depend.

Unsaturated Compounds.—Whereas methyl, or methane minus *one* hydrogen, cannot exist alone, substances exist which have been formed from the saturated compounds by the loss of *two* or *four* combining weights of hydrogen. Under certain circumstances these can again take up this hydrogen, and they are, therefore, called unsaturated compounds.

No such compound, however, is formed from methane; they first begin with ethane. The hydrocarbon C_2H_4, which contains two hydrogens less than ethane, C_2H_6, is called ethylene, and that containing four less, C_2H_2, is called acetylene.

Ethylene is a colourless gas whose critical temperature is 10°, and which forms a constituent of ordinary coal gas. In the latter it is very valuable, since it burns with a strongly luminous flame, and therefore very materially aids in producing the luminosity of the gas flame. In consequence of its containing a comparatively large amount of carbon, the pure gas burns in the air with a somewhat smoky flame.

Ethylene is most easily prepared from ethyl alcohol by treating the latter with dehydrating agents (concentrated sulphuric acid). The equation of the reaction is $C_2H_6O = C_2H_4 + H_2O$. The greater part of the alcohol vapour which is carried over, and of the by-products formed in the reaction, is removed by passing the gas through water.

If ethylene is brought together with chlorine or bromine, the two substances unite directly to form the compounds $C_2H_4Cl_2$ and $C_2H_4Br_2$ respectively. These are saturated compounds, derivatives of ethane, C_2H_6, in which two hydrogens are replaced by chlorine or bromine; they may also be obtained directly from ethane by replacing its hydrogen by halogen. The compounds formed, ethylene chloride and ethylene bromide, are oily liquids; on account of this reaction, ethylene has also been called olefiant (oil-forming) gas.

Acetylene is a colourless and odourless gas whose importance has in recent times become greatly enhanced by reason of its application as an illuminant. It has the composition C_2H_2, and contains, therefore, four hydrogens less than ethane; it can, accordingly, unite with four combining weights of chlorine or bromine to form the compounds $C_2H_2Cl_4$ and $C_2H_2Br_4$ respectively, which can be regarded as substitution compounds of ethane. Of the two reactions, however, only the second takes place smoothly, since acetylene and chlorine interact with spontaneous explosion.

Acetylene is now prepared in large quantities by the action of water on calcium carbide. The latter is a substance produced by the action of coke on lime at very high temperatures (in the electrical furnace), and has the composition CaC_2; the formation of acetylene takes place according to the equation $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$.

Acetylene burns in air with a smoky flame, which becomes white and luminous when special burners are employed, in which a very thin or flat jet of gas can burn with abundant access of air. The illuminating power of this flame is very great, so that acetylene can be advantageously employed for illuminating purposes, especially where the simplicity of the generating apparatus is a consideration. The latter consists of an arrangement similar to that described on p. 86, the purpose of which is to allow the water to come into contact with the calcium carbide only in proportion as the gas is consumed.

The great illuminating power of the acetylene flame is due to its high temperature; the latter is due to the fact that acetylene is a substance which is formed from its elements with great absorption of energy, so that in the further transformations, this excess of energy is set free as heat. For, the heat of combustion of acetylene amounts to 1297 *kj*, whereas that of the carbon and hydrogen contained in it only amounts to 1012 *kj*. The difference of 285 *kj*, therefore, becomes free, in addition to the heat of combustion of the elements, and hence the high temperature.

Connected with this is the fact that acetylene is an explosive substance. If in a fairly large amount of acetylene the decomposition of the gas into its elements is brought about at any point, the temperature at the point of reaction will rise and can raise the temperature of the neighbouring portions of acetylene to the temperature of rapid decomposition. This process spreads, and thus the whole amount of the gas suddenly decomposes.

Experiments made on this point, in which the decomposition was initiated by means of electric sparks or fulminating pellets, have given the following results. Acetylene under ordinary atmospheric pressure cannot be made to explode completely. By the means employed, the neighbouring masses of the gas, it is true, are decomposed, but the decomposition is not propagated.

Propagation of the decomposition begins to occur only at a pressure of about 2 atmospheres. From this pressure onwards, and the more so the higher the pressure, acetylene becomes an explosive substance, undergoing decomposition with great violence when decomposition is started by any means at some point. The same property is exhibited by liquid acetylene. Since the critical temperature of this gas is 37° and the critical pressure 68 atm., the liquefaction of the gas can be easily accomplished. This operation is without any great danger if carried out at very low temperatures, in which case only slight pressures have to be applied, but at higher temperatures, with correspondingly greater pressures, it becomes on the whole very dangerous, and has claimed several victims.

Connected with the great absorption of energy in the formation of acetylene from its elements, is the fact that it is formed from the latter at very high temperatures (*vide* p. 327). For example, if an electric current be allowed to pass between two carbon poles in a space in which hydrogen is present (Fig. 99), the latter combines with the carbon with formation of acetylene.

The detection of acetylene depends on its power of yielding precipitates with a solution of a monovalent salt of copper, or of a silver salt in excess of ammonia, these precipitates being the carbon compounds or carbides of the respective metals. The silver precipitate is white, the copper one red. In the dry condition both explode violently; on being treated with acids they again yield up the acetylene.

Coal Gas.—The combustible gas which is used for heating and illuminating purposes, and which, under the name of coal gas, is so widely applied, is obtained by the dry distillation of coal rich in hydrogen. The coal is heated in tube-shaped retorts, and the hydrogen thereby combines with part of the carbon to form volatile compounds; the rest of the carbon and the ash of the coal remain behind and form coke, which is of value as a fuel.

The volatile products are a mixture of very diverse substances, which can be divided, in the first instance, into three chief portions, according to varying volatility. As least volatile portions, there first separate the *gas liquor* and the *gas tar*. These two are not soluble in one another, and can, therefore, be separated mechanically. The gas liquour is, essentially, an aqueous solution of ammonium carbonate and other ammonium salts; it is worked up to obtain ammonia by distilling it with the addition of lime, and converting the ammonia which is evolved into ammonium sulphate with sulphuric acid.

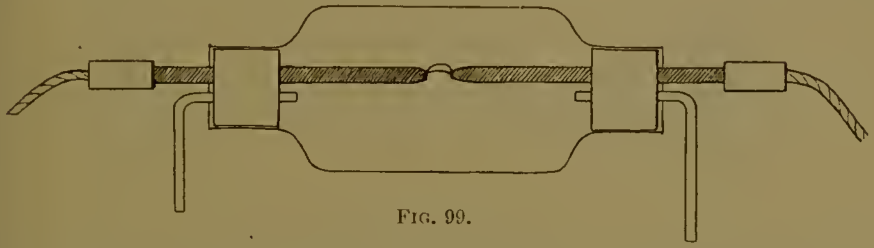


FIG. 99.

Gas tar is a mixture of hydrocarbons and their derivatives. It serves as the source for obtaining benzene, naphthalene, and anthracene —hydrocarbons which are of the greatest importance for the preparation of artificial dye stuffs and medicaments; from it there are also obtained phenol (carbolic acid) and compounds related to it, which are used for purposes of disinfection and for the preparation of smokeless gunpowder. Numerous other substances are present in gas tar, which are used as crude material, so that it may be designated as the most important starting substance in the chemistry of the organic compounds.

The working up of the gas tar is also carried out essentially by fractional distillation, with the aid of lime and sulphuric acid. The details of this belong to the chemical technology of the organic compounds.

The *gas*, which is evolved at the same time, is freed by cooling and washing from the tar; and by passing it over a mixture of lime and oxide of iron, the sulphur compounds it contains, and which, by reason of the formation of sulphur dioxide would have a baneful effect when the gas is used in inhabited rooms, are removed; it is then stored in large gas-holders for distribution through the network of tubes to the individual consumers.

Coal gas varies considerably in composition, according to the material used for its preparation. Its chief constituents are hydrogen, methane, carbon monoxide, and some hydrocarbons richer in carbon, especially ethylene, benzene, and naphthalene. The latter two compounds are respectively liquid and solid at the ordinary temperature; they can mix with the gas, therefore, only in amount corresponding to their vapour pressure, and again separate out when the gas experiences any considerable lowering of temperature.

* To give an idea of the composition of ordinary coal gas, we give here the results of an analysis in which the constituents are stated in *parts by volume* :—

Hydrogen	49·6
Methane	29·8
Carbon monoxide	9·6
Hydrocarbons	5·0
Carbon dioxide	2·7
Nitrogen	2·6
Benzene vapour	0·7

The "hydrocarbons" consist chiefly of ethylene.

At first coal gas was chiefly prepared for illuminating purposes, and the chief attention was therefore directed to obtaining a gas rich in ethylene and other "heavy hydrocarbons." Such can be obtained only from certain expensive kinds of coal, and the product, therefore, the coal gas, is correspondingly dearer. Meanwhile, the gas has been found to be very convenient for heating purposes and for driving engines (gas engines); for these purposes, however, a strongly luminous gas is troublesome rather than useful. Since in the meantime, also, means have been found of obtaining very considerable illumination from feebly luminous gas (incandescent light), it can only be a question of time till the gas-works begin to chiefly manufacture a gas with great heat effect without consideration of the illuminating power, and one which can be prepared much more cheaply than the present coal gas.

* A feebly luminous gas can be made strongly luminous by adding to it (best done immediately before its consumption) a small quantity of the vapours of complex hydrocarbons (benzene or naphthalene). Such "carburetted" gas is already much used. It is only necessary to conduct the gas through a vessel in which the above-named substances are contained, the vapour pressure of these being, at mean room temperature, great enough to effect a sufficient carburetting.

* Another still more advantageous method consists in the use of

mantles of solid substances which are raised to incandescence in as hot a flame as possible. The details of this will be given later (cf. Thorium, Chap. XLI.).

In the laboratory coal gas is used very extensively for heating. The burner used for this purpose was invented by R. Bunsen in 1855. It consists (Fig. 100) of a jet fastened to an iron base, from which the gas streams into a wider, upright tube, which is furnished with lateral draught-holes beside the jet. In the tube the coal gas is mixed with air, and the mixture burns at the mouth of the tube with a hot and very slightly luminous flame, which deposits no soot on a cold object when introduced into it. This is due to the fact that by means of the draught-holes the gas is mixed with as much air as is necessary for the oxidation of the hydrogen and the conversion of the carbon present into carbon monoxide.

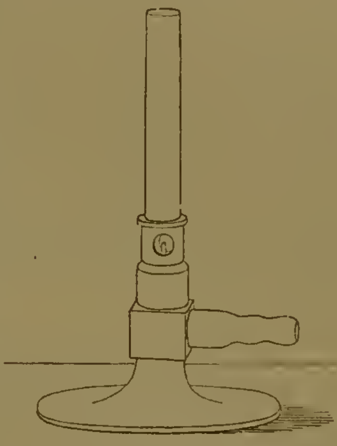


FIG. 100.

Numerous other forms of burner, which have been adapted for various purposes, have been made on the principle of the Bunsen burner. In Fig. 101 is shown the construction of a flat burner for heating larger vessels.

The mixture of gas and air which issues from the burner is explosive; the velocity with which it issues is, however, usually so great that the combustion is propagated backwards more slowly than the gas moves forward. If the flow of gas is reduced below a definite point, the state of matters is reversed, and the burner "strikes back." To avoid this, the access of air must be reduced at the same time, and some forms of burner are so constructed as to do this automatically.

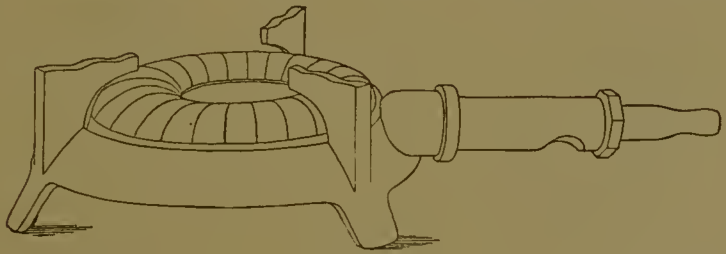


FIG. 101.

The flame of a Bunsen burner consists of two parts: an inner, green hollow cone, and an outer, blue mantle. In the hollow cone the combustion of the hydrogen and of the carbon to carbon monoxide essentially occurs; in the outer mantle the combustion to dioxide is completed. For this reason, the inner cone has a reducing action on substances introduced into it, whereas in the outer edge of the mantle an excess of oxygen is present. These differences are made use of for the purposes of chemical analysis.

Oxalic Acid.—By the oxidation of many carbon compounds there is formed an acid of the composition $H_2C_2O_4$, which, by reason of its manifold importance, we shall also mention here. It is called *oxalic acid*, and since both its hydrogens are replaceable by metals, it is a dibasic acid.

Oxalic acid is a white crystalline substance, which readily dissolves in water, and gives an acid reaction; it is found to be an acid of medium strength. The ordinary crystallised oxalic acid contains water of crystallisation, and its composition is represented by the formula $H_2C_2O_4 + 2H_2O$. With bases it forms two series of salts, acid and normal, and most of these are difficultly soluble in water. Of these salts, the most important are the acid potassium salt and the normal calcium salt.

The former, having the composition KHC_2O_4, occurs in many plants possessing an acid taste, and can be obtained crystalline by the evaporation of the juice pressed out from these. For its preparation there was formerly chiefly used the wood-sorrel (*oxalis*), from which the name oxalic acid is derived; likewise, the potassium salt is called *salt of sorrel.*

The neutral calcium salt CaC_2O_4 is very difficultly soluble in water. It occurs in almost all plants, being found in the cells as very characteristic hydrated crystals which have the appearance of envelopes. In analytical chemistry it is of importance from the fact that it is the form in which the calcium compounds are detected qualitatively and determined quantitatively. As reagent for this purpose, the ammonium salt of oxalic acid is mostly used.

On being heated, oxalic acid first decomposes into formic acid and carbon dioxide, $H_2C_2O_4 = HCOOH + CO_2$, but this decomposition can be accomplished only with great care or with the help of suitable catalysers. On heating more strongly, the formic acid also decomposes, and there are obtained carbon dioxide, carbon monoxide, and water: $H_2C_2O_4 = CO_2 + CO + H_2O$. The salts of oxalic acid on being heated are converted, with evolution of carbon monoxide, into carbonates, which in some cases decompose further: *e.g.* $CaC_2O_4 = CaCO_3 + CO = CaO + CO_2 + CO$.

Further, oxalic acid decomposes into carbon monoxide and carbon dioxide when treated with dehydrating agents, such as concentrated sulphuric acid. This reaction is made use of for the convenient preparation of carbon monoxide; oxalic acid or a salt of this is warmed with concentrated sulphuric acid, and the escaping gases passed through a wash-bottle with caustic soda. The carbon dioxide is absorbed by this, and pure carbon monoxide is obtained.

Oxalic acid is fairly sensitive to oxidising agents, and is readily oxidised by them to carbon dioxide: $H_2C_2O_4 + O = 2CO_2 + H_2O$.

This reaction is also used in analytical chemistry, and we shall later have occasion to return to it (Chap. XXVIII.).

Carbon Disulphide.—When charcoal is heated in a current of sulphur vapour, a compound of the two elements is formed. It has the composition CS_2, for its vapour density is 76, and analysis shows it to contain 64 of sulphur to 12 of carbon.

Carbon disulphide is a colourless liquid, whose density is about 1·3, and which boils at 47°. In the pure state it is almost colourless. Ordinary carbon disulphide, owing to the presence of other sulphur compounds, has generally rather a bad smell. It can be purified by shaking with metallic mercury and distilling.

Carbon disulphide refracts and disperses light very strongly; its indices of refraction (at 17°), for the most important rays, are:—

	A	B	C	D
Wave length	7604	6867	6562	5890
Index of refraction	1·61136	1·61756	1·62086	1·63034

	E	F	G	H
Wave length	5270	4861	4308	3968×10^{-8} cm.
Index of refraction	1·64320	1·65529	1·67975	1·70277

For this reason it has often been attempted to use it for optical apparatus, *e.g.* for prisms in spectroscopes. This, however, has not met with success, since the great expansion by heat very readily causes disturbances; further, carbon disulphide is somewhat sensitive to light, and when exposed to light for a lengthened period it decomposes and its properties change.

Carbon disulphide is a good solvent for many substances; in this rôle, we have already met with it in the case of sulphur and iodine. It also readily dissolves fats and resins, a fact on which many technical applications of it depend.

By reason of being composed of two combustible elements, carbon disulphide can be ignited, and it burns in the air with a blue flame, with formation of sulphur dioxide and carbon dioxide. Its temperature of ignition is very low, so that the vapour of carbon disulphide can be ignited under circumstances in which other combustible substances are far from taking fire. Corresponding care must, therefore, be observed in using this compound.

Mixed with nitrous oxide, carbon disulphide burns with a flame which is especially rich in ultraviolet and violet rays, and which, therefore, under certain circumstances, is used for photochemical purposes. The sulphur dioxide thereby formed, however, is a hindrance to its general use.

Carbon disulphide is formed from its elements with absorption of −120 *kj*. Its heat of combustion amounts to 1320 *kj*, whereas that of the elements is only 1200 *kj*. In very special circumstances, therefore, it may be caused to decompose explosively; this, however, is difficult, and, as a rule, it exhibits no explosive properties.

From carbon disulphide an acid is derived which bears the same relation to it as carbonic acid does to carbon dioxide. Only, the acid is not composed of carbon disulphide and *water*, but of carbon disulphide plus *sulphuretted hydrogen*, and has, therefore, the composition H_2CS_3.

From this example it will be seen that besides the oxyacids there are others which have a similar composition to these but contain sulphur in the place of oxygen. These are called *thio-acids*, and the above acid, *thiocarbonic acid*, is such an acid, as can be seen by writing the two formulæ side by side :—

Anhydride	CO_2	CS_2
Acid	H_2CO_3	H_2CS_3
Sodium salt	Na_2CO_3	Na_2CS_3.

The sodium salt is obtained by dissolving carbon disulphide in sodium sulphide, in accordance with the equation $CS_2 + Na_2S = Na_2CS_3$. From a solution of this salt, thiocarbonic acid can be precipitated by addition of an acid. Unlike carbonic acid, it only slowly decomposes, so that it separates out as an oily liquid, only slightly soluble in water. This is, however, not stable, but slowly decomposes into carbon disulphide and sulphuretted hydrogen: $H_2CS_3 = H_2S + CS_2$.

The thiocarbonates have attained to a certain importance from the fact that carbon disulphide has been found to be a means for destroying the phylloxera. Whereas carbon disulphide is so volatile as to be inapplicable for this purpose, the thiocarbonates are suitable.

Under the influence of the carbon dioxide in the air and in the soil, these are converted into carbonates, carbon disulphide and sulphuretted hydrogen being split off: $Na_2CS_3 + CO_2 + H_2O = Na_2CO_3 + H_2S + CS_2$. The process takes place slowly, but still with such rapidity that the amount of carbon disulphide present at each moment is sufficient to exercise the desired action.

Carbon Oxysulphide.—In various ways, most easily by the decomposition of the thiocyanates (*vide infra*) with sulphuric acid, a compound, COS, is formed which can be regarded as an intermediate compound between carbon dioxide and carbon disulphide. It is a gas which is readily absorbed by water, with which it slowly interacts, with formation of carbonic acid and sulphuretted hydrogen : $COS + 2H_2O = H_2CO_3 + H_2S$. This reaction is greatly accelerated by the addition of a base, the salts of the two acids being formed.

Carbon oxysulphide smells somewhat like sulphuretted hydrogen, and readily burns in the air with a blue flame, forming carbon dioxide and sulphur dioxide.

Cyanogen.—When carbon and nitrogen are exposed to very high temperatures, such as exist, for example, in the electric arc (Fig. 99,

p. 407), these two elements combine to form a gas which, in accordance with its composition and density, 52, has the formula C_2N_2. On account of the blue compounds which it yields with iron, and which have been known for long, this substance has received the name cyanogen (producer of blue substance).

Cyanogen is a colourless gas with peculiar smell and poisonous action on the organism. Its critical temperature is 124°, its critical pressure 62 atm. In its solubility in water it resembles carbon dioxide, to which it also approximates with respect to its density (52 as compared with 44).

Cyanogen can be ignited in the air, and burns, with a characteristic flame of red-violet colour, to carbon dioxide and nitrogen. A considerable amount of heat is thereby developed, amounting to more than would be given by the corresponding amount of charcoal. Cyanogen, therefore, also belongs to those compounds which are formed with absorption of energy, and whose spontaneous formation occurs at very high temperatures. It is thus formed on all occasions where carbon and nitrogen come together at a high temperature, *e.g.* in the blast furnace in the preparation of iron. The heat of combustion of cyanogen is 1087 *kj*, whereas that of two carbons amounts to 812 *kj*; in the formation of the gas, therefore, 275 *kj* are absorbed.

In its chemical relations, cyanogen is analogous to the halogens, and forms a whole series of compounds in which the group CN behaves like chlorine or iodine.

In the first place, there should be mentioned the hydrogen compound HCN, *hydrocyanic acid* or *prussic acid*. This compound is obtained by decomposing the metallic cyanides with an acid, just as hydrochloric acid is obtained from common salt. The metallic cyanides, in turn, are formed by allowing carbon, nitrogen, and the respective metals, or their carbonates, to act on one another at a high temperature. A more exact description of what takes place here will be given later under the metals.

For the liberation of hydrocyanic acid from its salts, a strong acid is not required, for hydrocyanic acid stands at the outermost limit of the weak acids. The aqueous solution scarcely exhibits an acid reaction, and dissolved metallic cyanides can be decomposed even by such weak acids as carbonic acid. In consequence of this the metallic cyanides, when exposed to the air (containing carbonic acid), smell of hydrocyanic acid, and the aqueous solutions are partially dissociated hydrolytically and react alkaline (p. 247).

In the pure state, hydrocyanic acid is a colourless liquid which boils at 27° and solidifies at − 15°. It is a highly poisonous compound, which even in small amounts quickly acts fatally. The cause of its poisonous action is probably due to its being a retarding catalyser for many physiologically important processes, especially the oxidation in the organism.

Hydrocyanic acid can be detected even in small quantities by its smell, which recalls that of bitter almonds. The reason of this is that in bitter almonds a substance, amygdalin, is present which decomposes under the influence of a catalyser or ferment, which is also present in other cells, into hydrocyanic acid, sugar, and a volatile oil, oil of bitter almonds. Crushed bitter almonds, therefore, smell of hydrocyanic acid when, owing to the destruction of the cells, these two substances, amygdalin and the ferment, come together.

Whereas the aqueous solution of hydrocyanic acid contains exceedingly few ions, the soluble metallic compounds, which, in a corresponding manner to the chlorides, are obtained by the action of hydrocyanic acid on the oxides or hydroxides of the metals, are normally dissociated into their ions. Thus, the solution of one of the best known metallic cyanides, potassium cyanide, KCN, contains the ions $K^{\cdot}$ and CN'. The ion CN' has a great resemblance to the ions of the halogens; with argention, for example, it gives a difficultly soluble compound, which is deposited as a white precipitate, very similar to silver chloride, when cyanidion and argention (*e.g.* from potassium cyanide and silver nitrate) are brought together in solution.

* For the purpose of detecting cyanogen compounds, use is made of various very sensitive reactions, which may be shortly mentioned here, although their theory cannot be given till later (Chap. XXVII.). The liquid to be investigated, after being made alkaline by addition of caustic soda or potash, is warmed with a ferric salt, and hydrochloric acid then added. If cyanidion was present, a dark blue precipitate is obtained, or, in the case of very small quantities, a blue or green-blue coloration. The blue iron compound is hereby formed which has given the name to the whole group.

* Or, the liquid, with addition of yellow ammonium sulphide, is evaporated to dryness, the residue dissolved in a drop of water, and ferric chloride added. If cyanidion was present, a blood-red coloration is produced. This depends on the formation of thiocyananion by means of the sulphur from the ammonium sulphide, and this gives the above reaction with ferric chloride. A knowledge of this test is of practical importance by reason of the not infrequent cases of poisoning with prussic acid, or with cyanides.

Relation of the Cyanogen Compounds to the Ammonia Derivatives of the Carbon Compounds.—When hydrocyanic acid is mixed with strong hydrochloric acid, a reaction takes place, and ammonium chloride and formic acid are produced. The reaction can be looked upon as essentially a taking up of water: hydrocyanic acid and water yield formic acid and ammonia, in accordance with the equation $HCN + 2H_2O = HCOOH + NH_3$.

This reaction recalls the conversion of the amides into the ammonium salts of the corresponding acids (p. 343), but it differs from it by the fact that *two* moles of water are taken up instead of one.

In suitable cases, therefore, there are two stages of dehydration of the ammonium salts: the first yields the amide, the second a compound for which the general name *nitrile* has come into use. In the present case we have

Ammonium formate	$HCOO \cdot NH_4$
Amide of formic acid, or formamide	$HCO \cdot NH_2$
Nitrile of formic acid, or hydrocyanic acid	HCN

As a matter of fact, hydrocyanic acid can be obtained from ammonium formate by means of strongly dehydrating agents.

A similar series shows cyanogen itself to be the nitrile of oxalic acid—

Ammonium oxalate	$C_2O_4(NH_4)_2$
Amide of oxalic acid, or oxamide	$C_2O_2(NH_2)_2$
Nitrile of oxalic acid, or cyanogen	C_2N_2.

Here, also, we may pass through the series not only by dehydration from above downwards, but also by absorption of water from below upwards.

The further extension of these indications belongs to organic chemistry.

Cyanic Acid.—Of the oxyacids of cyanogen which would correspond to the acids from hypochlorous up to perchloric acid, only the first member is known. By analogy, this should be called hypocyanous acid, since its composition is represented by the formula HOCN; since, however, no other oxygen compound is known, it is called cyanic acid.

Cyanic acid is a very unstable compound. It is obtained by heating another compound, cyanuric acid, which has the same composition but three times the molar weight, $H_3O_3C_3N_3$. From the vapour of this substance there is deposited, in accordance with the law of the precedence of the unstable forms, not the stable cyanuric acid, but the unstable cyanic acid, HOCN. The condensation of this compound, however, must be carried out at as low a temperature as possible, for, on gently heating, cyanic acid is converted, with strong development of heat, sometimes with explosive violence, into more stable forms, of which there are several. It is a colourless liquid with a strong smell, resembling that of acetic acid.

In aqueous solution, also, cyanic acid is not stable, but is quickly converted, by absorption of water, into acid ammonium carbonate. This process is represented by the following equation: $HOCN + 2H_2O = (NH_4)HCO_3$. For this reason, a solution of a cyanate on being acidified effervesces and evolves carbon dioxide as if a carbonate were present. After the reaction, an ammonium salt is present in the solution.

Although cyanic acid is very unstable, the cyanates are mostly very stable compounds. They are formed, for example, with great readiness by exposing the cyanides to the action of oxidising agents. On this account, fused potassium cyanide is a powerful reducing agent, which withdraws the oxygen from various metallic oxides and converts them into metals. This reduction can be shown with especial ease in the case of lead oxide and bismuth oxide; under the liquid salt, the metals fuse together into drops which look bright like mercury. The same reaction is made use of for obtaining cyanates, especially potassium cyanate, from the corresponding cyanides; as oxide, pyrolusite (p. 54), is mostly employed.

A specially interesting reaction of cyanic acid is the transformation which its ammonium salt undergoes, and which led to the synthesis of urea (p. 393).

Ammonium cyanate has the formula NH_4OCN, and contains the same elements in the same proportions as urea, for both have the total formula CH_4N_2O. If, however, it is attempted to prepare ammonium cyanate, urea is obtained in its place. In the meantime, however, it has been shown that true ammonium cyanate possessing the expected properties of this substance exists; but it is very unstable, and rapidly undergoes transformation into the isomeric compound urea.

This reaction takes place so soon as the ions OCN' and $NH^{\cdot}_4$ come together in aqueous solution. On mixing any cyanate, *e.g.* potassium cyanate, and an ammonium salt, *e.g.* ammonium sulphate, in aqueous solution and evaporating the solution, a residue of potassium sulphate and urea is obtained, which can be readily separated by means of alcohol.

Thiocyanogen.—If potassium cyanide or other cyanide is fused with sulphur or a sulphur compound, or even if a solution of one of these salts is heated with sulphur, the latter is taken up and a solution of a salt is obtained of the composition MSCN, in the case of potassium, therefore, KSCN. This compound, which gives a very pronounced blood-red or brown-red coloration with ferric salts, is called *potassium thiocyanate;* it is the potassium salt of a corresponding *thiocyanic acid*, HSCN, and its solution contains, besides potassion, thiocyananion, SCN'.

The composition of these compounds is similar to that of the cyanic acid compounds, only that sulphur is present in the place of oxygen. Thiocyanic acid is distinguished from cyanic acid by its much greater stability.

From the barium salt, by precipitation with sulphuric acid (p. 290), an aqueous solution of thiocyanic acid can be obtained; this is a very acid liquid whose acid properties are not greatly inferior to those of hydrochloric acid. In the free state, thiocyanic acid is unknown; on attempting to prepare it, a rather complex decomposition occurs in which carbon oxysulphide, COS, is formed (p. 412). The formation of this latter compound takes place directly by splitting off ammonia with the aid of water, a reaction which can be represented by the equation $HSCN + H_2O = COS + NH_3$. The decomposition occurs on heating potassium thiocyanate with a medium strong solution of sulphuric acid.

With regard to its similarity to the halogens, thiocyananion, SCN', is quite analogous to cyananion ; it, also, gives with argention a white precipitate, which, in its external appearance, cannot be distinguished from silver chloride or silver cyanide.

Corresponding to the gaseous cyanogen, however, no thiocyanogen is known. There are substances, it is true, which have the composition SCN, but these are certainly polymeric compounds of the formula $(SCN)_n$, where *n* is a number probably greater than 3. They belong, therefore, to quite a different group of substances, which are generally treated in organic chemistry.

CHAPTER XVII

SILICON

SILICON stands to carbon in the same relation as sulphur to oxygen. The two elements are similar in many respects, but differ more from one another than, for example, chlorine, bromine, and iodine do.

Silicon, like carbon, occurs in several forms, of which an amorphous and a crystalline form are accurately known. Amorphous silicon is obtained by conducting its chlorine or fluorine compound over heated potassium; the metal unites with the halogen, and the silicon is set free. The soluble potassium salt formed is removed by washing with water, and the silicon is left behind as a greenish-brown powder. This is amorphous, and has the tendency to pass into the colloidal state; if, therefore, the washing is continued to a certain point, the silicon goes into a sludge and begins to pass through the filter.

Amorphous silicon is more easily obtained by heating its oxygen compound, finely powdered quartz, with magnesium powder. The magnesium combines with the oxygen of the silicon dioxide, forming magnesium oxide, and the silicon is liberated. The latter can be obtained pure by extracting the product with dilute acid, in which the magnesium oxide but not the silicon dissolves.

At a high temperature, silicon melts; and on solidifying, crystalline silicon is formed as a grey mass with a metallic lustre. The crystallisation is greatly facilitated by the addition of a metal such as zinc; the zinc can be removed by treating the product with dilute acids.

Amorphous silicon can be set on fire in the air, but its combustion is very incomplete, because the non-volatile silicon dioxide formed prevents further combustion. Crystalline silicon does not noticeably change in the air even at a red heat. Silicon is soluble in caustic soda on heating, the silicon thereby taking up oxygen from the water and passing into an acid, silicic acid, or rather into its sodium salt. The hydrogen of the water escapes as a gas.

The combining weight of silicon has been determined by the analysis of its halogen compounds, and amounts to Si = 28·4.

Silicon Dioxide.—By far the most important compound of silicon is silicon dioxide or the anhydride of silicic acid. It has the formula SiO_2, or a multiple of this, and occurs in enormous quantities in nature both in the free state and as salts. The largest part of the earth's surface is composed of silicon dioxide, or of its compounds ; over a quarter of the solid crust of the earth is formed by silicon.

Silicon dioxide occurs in several varieties, two crystalline and one amorphous. It is most widely distributed in the crystalline form as quartz, rock crystal, amethyst, smoky quartz. These and various other minerals are, chemically, the same substance, and appear to be different only by reason of the impurities to which the difference in colour is due.

The purest form is rock crystal, which crystallises in six-sided prisms and is colourless. The crystals possess the property of rotating the plane of polarised light when this is passed through parallel to the axis of the prism. In some crystals, the rotation is to the right, in others to the left, and the sense of the rotation is closely related to a one-sided crystallographic formation, by means of which right and left crystals can also be distinguished. The difference is seen in the hemihedral faces (Fig. 102) ; a right and a left crystal can no more be superposed on one another than can a right and a left-hand glove.

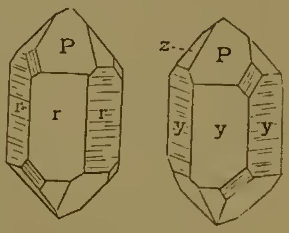


FIG. 102.

While rock crystal is clear as water, smoky topaz, or, better, smoky quartz, is brown to black, amethyst violet, ordinary quartz whitish and turbid. There are also yellow, rose-red, and other coloured varieties.

Quartz forms a constituent of many rocks, especially of granite, gneiss, etc. By the action of water and carbonic acid, these rocks are disintegrated as well as partially changed chemically (*vide infra*), and the quartz grains are left detached. These are borne away and broken up by the rivers, and finally reach the sea in the form of *quartz sand*. On the sea-bottom the sand masses frequently become united again by means of a binding material (limestone or iron oxide) to solid masses ; sandstone, which forms extensive mountain ranges and consists of quartz grains, has been so formed.

Quartz has the density 2·66, and a hardness 7, *i.e.* it represents the third hardest grade after the diamond. Quartz is used, therefore, for grinding metal (grindstones and whetstones) and glass.

The other crystalline form of silicon dioxide is called *tridymite*. It occurs almost solely in microscopic crystals as a constituent of rocks, and is less dense than quartz (2·3 as compared with 2·66).

Amorphous silicon dioxide occurs as a mineral in various rocks. The most wide-spread and best known form is flint, which forms rounded masses in chalk, and is coloured by organic substances, yellow, brown, or black. It is but slightly inferior to quartz in hardness, and by reason of its conchoidal fracture sharp edges can easily be formed on it. In prehistoric times, when the methods of obtaining and working metals were unknown, this mineral was used for making knives, axes, and arrow heads. It is the stone which was chiefly employed in the "Stone Age."

Other forms of amorphous silicon dioxide are opal, chalcedony, jasper, etc., which differ essentially only in structure and layer formation, but do not differ chemically. In chemical operations, silicon dioxide is usually obtained amorphous, and it is not very easy to cause it to crystallise; nevertheless, both crystalline forms have already been artificially prepared.

Silicic Acid.—Silicon dioxide is the anhydride of an acid, silicic acid, or rather of a whole series of acids which can be compounded of the elements of silicon dioxide and water. The relations are similar to those obtaining in the case of the phosphoric acids, only more diverse.

As extreme member of the series of the different silicic acids, there may be regarded the tetrabasic orthosilicic acid, $Si(OH)_4$; $SiO_2 + 2H_2O = Si(OH)_4$. It is not known in the pure state, but in the form of its salts.

By loss of water, it passes into the dibasic acid $SiO(OH)_2$, the composition of which corresponds to that of carbonic acid.

Other silicic acids are formed by the union of several combining weights of the ortho-acid with loss of water. From $2Si(OH)_4$ there are formed $Si_2O_7H_6$, $Si_2O_6H_4$, $Si_2O_5H_2$. In a similar manner, corresponding "pyro-acids" can be derived from several combining weights of silicic acid.

Unlike the phosphoric acids, the different silicic acids cannot be distinguished from one another by any reactions; that these different types exist can be concluded only from the existence of the corresponding salts which occur naturally in the crystalline form.

These salts of silicic acid or silicates are all practically insoluble in water, with the exception of the silicates of the alkali metals, which can be dissolved, and whose solutions bear the name of water glass. These salts are readily obtained by fusing quartz with the hydroxides or carbonates of the alkali metals. From these solutions, the silicic acid can be set free by other acids.

If the mixing of an alkaline silicate with acid, *e.g.* hydrochloric acid, be carried out in concentrated solution, the silicic acid separates out in friable, gelatinous masses. If, however, dilute solutions are employed and an excess of acid, no precipitation is obtained, but the solution remains clear and apparently unchanged. This looks as if the silicic acid were difficultly soluble, so that it is partially precipitated from concentrated solutions while it remains dissolved in much water. This is, however, not the case; the solution of silicic acid which is formed is no true solution, but the silicic acid is present in the *colloidal* state.

This is seen when the liquid is subjected to dialysis, *i.e.* when it is placed in a vessel whose walls are formed entirely or partially of parchment paper or of bladder, and the vessel placed in pure water. The salt which is formed and the excess of acid then pass by diffusion freely through the membrane, while the silicic acid, like all colloidal substances, is retained. If the experiment is continued for a number of days with frequent renewal of the water, all the salts, as far as can be detected, will finally diffuse away, and the solution in the dialyser will contain only silicic acid.

This silicic acid shows the characteristic properties of "colloidal solutions" or "pseudo-solutions." On evaporating to dryness no crystals are formed, but there is left an amorphous, glassy mass which only incompletely re-dissolves in water. Boiling and freezing point differ only exceedingly slightly from those of water; special chemical reactions cannot be detected. By addition of various substances, especially of salts, the liquid solidifies to a jelly, especially if it has been somewhat concentrated by evaporation in the cold.

In nature silicic acid occurs very often in such a form. It gets into the natural waters from the silicates when these are decomposed by carbonic acid. Under suitable conditions, the silicic acid crystallises from such solutions; smoky quartz, especially, has probably been formed in this way. For, since it owes its coloration to organic substances which are destroyed by ignition, it must have been formed at a low temperature, and, during the period of its existence, can never have been subjected to a red heat. The way in which it occurs, also, makes its formation from solutions probable.

Silicic acid, or quartz, is extensively applied in the arts. Sandstone is a greatly valued, because easily worked and resistant building material; quartz sand is used as an addition to mortar and for grinding. By fusing quartz with the carbonates of the alkali and alkaline earth metals, amorphous, transparent masses are obtained, which, as *glass*, find very manifold application. Colourless rock crystal is used as a cheap ornamental stone, and also, on account of its rotating the plane of polarised light and of its transparency for light of all wavelengths, in the construction of optical instruments. For spectacle glasses, also, quartz is used, since, on account of its great hardness, it loses the polish less easily than glass lenses.

Geological Reactions.—Of all chemical processes occurring on the earth's surface, the interaction of the naturally occurring silicates with water and carbonic acid is the one which, quantitatively, stands pre-eminent. The primitive rocks of the earth were essentially silicates; the carbon, in all probability, was present as carbonic acid. This corresponds to the equilibrium at comparatively high temperatures, which must be assumed to have prevailed originally on the earth.

At lower temperatures the equilibrium changes in such a way that carbonic acid displaces silicic acid from its salts. In other words, a system consisting of carbonates and free silicic acid, or silicon dioxide, is, at lower temperatures, more stable than the system carbon dioxide and silicate. For this reason, the silicates of the various primitive rocks are subjected to uninterrupted chemical processes, to which is added a mechanical disintegration by the action of water, of changing temperature, and of the wind. The consequence of this is that the silicates which are decomposable under these circumstances are transformed, the non-decomposable are disintegrated, and carbonates are formed from the constituents of the transformed rocks.

The silicates of the alkali metals, especially, undergo this decomposition. These, it is true, do not occur in the free state in nature, but only as double silicates combined with the silicates of other metals. They become thereby more stable, but still not absolutely resistant, and are therefore decomposed.

The alkali metals pass into the waters as soluble carbonates, and are partially retained in the soil by absorption. This retention is specially great in cultivated soil, where it is conditioned, partially at least, by the presence of organic substances. Another portion passes on into the sea. This is also the destination of the alkaline earth metals, which are there deposited chiefly as carbonates.

Of the dissolved silicic acid, a considerable portion also reaches the sea, and is there utilised by various animals for building up their skeleton. Another portion forms hydrated magnesium silicate with the magnesium of the rocks. This is a compound which, under certain circumstances, resists the action of water, and which is therefore formed when its constituents come together. The conversion of the original rocks into serpentine or steatite, as the hydrated silicate of magnesium is called in mineralogy, can constantly be recognised at various points.

Of the other metals which occur abundantly on the earth's surface, aluminium also is capable of remaining in combination with silicic acid, even under the existing conditions. Aluminium silicate is a very widely distributed constituent of the primitive rocks. In the decomposition by water and carbonic acid, or "weathering," aluminium silicate is not decomposed, but remains as an amorphous residue when the other constituents have been dissolved. The very finely divided mass is carried by the rivers to the sea if it has not previously been deposited at comparatively quiet spots as clay, potter's earth, or loam. On the sea bottom the deposited clay slowly hardens into slate and similar secondary rocks.

By means of these various transformations, a one-sided change takes place in the composition of the earth's crust, the tendency of which is to more and more increase the amount of carbon in the form of calcium and magnesium carbonate, while the silicic acid which before had formed salts with these metals is separated in the free state. By this process the amount of carbon dioxide in the air must also slowly become less. By the combustion of fossil fuel, it is true, a certain amount of the carbon which had been long removed from the air, is again given back to it, and in isolated localities where volcanic activity occurs at a comparatively small depth below the surface of the earth, the carbonates formed in the wet way also appear to undergo decomposition as a consequence of the rise of temperature, as is indicated by the streaming forth of carbonic acid at the places mentioned. Still these amounts of carbon, which are again put into circulation, are probably much less than the amounts which, in the form of carbonates, are withdrawn from circulation.

If we consider, now, that all organisms must have recourse to carbon for the building up of their body, we see that the slow diminution of the amount of floating carbon-capital which is taking place on the surface of the earth must exercise a great influence on the moulding of life. It can be regarded as highly probable that the essentially different state of affairs which, as may be concluded from the investigations of the geologists, prevailed in former periods were due to the influence of the larger amounts of carbon dioxide then present in the air, and that in the future also, organic life will undergo variation in such a sense that the continued diminution will be met in a suitable manner.

Halogen Compounds of Silicon.—When a mixture of silicon dioxide and charcoal is strongly heated in a current of dry chlorine, decomposition takes place, and there is obtained, besides carbon monoxide, a volatile substance which analysis and vapour density show to have the composition $SiCl_4$. The reaction, therefore, takes place in accordance with the equation $SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO$.

Whereas neither carbon nor chlorine alone can decompose silicon dioxide, the decomposition can be effected when both substances act together. The reason of this is that by the simultaneous action of the two substances, products are formed which are much more stable, or contain much less free energy, than when the substances act separately. For chlorine alone would yield free oxygen along with silicon chloride; charcoal alone, free silicon along with carbon monoxide; whereas, when they act together, the formation of substances with a large amount of energy, such as oxygen and silicon, is avoided. Of the principle which forms the basis of this reaction, use is frequently made.

Silicon chloride can also be obtained by the action of chlorine on amorphous silicon. It is a colourless liquid which boils at 59° and has the density 1·5. In moist air it fumes strongly, since it is very readily decomposed by water to hydrogen chloride and silicic acid: $SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl$. This reaction shows it to be the chloride of silicic acid.

If silicon is heated not in a current of chlorine but in one of hydrogen chloride, the latter is decomposed and a chlorine compound of silicon, which also contains hydrogen and has the composition $SiHCl_3$, is formed. On account of the similarity of this formula to that of chloroform (p. 400), the substance has been called silico-chloroform. It is a colourless liquid which looks like silicon chloride, and, like this, is also decomposed by water; it boils, however, somewhat lower, viz., at 36°.

Corresponding to these chlorine compounds, there are also bromine and iodine compounds which have an analogous composition, and which, in accordance with the general rule, have higher boiling points than the chlorine compounds, but which otherwise behave quite similarly and are obtained in a similar manner. Silicon iodide is a solid at the ordinary temperature, and passes into a liquid only at 120°.

Silicon Hydride.—A compound of the composition SiH_4 is obtained, mixed with much hydrogen, when magnesium containing silicon is dissolved in hydrochloric acid. Since it can be liquefied much more easily than hydrogen, it can be obtained pure by cooling sufficiently strongly. It possesses the property of igniting spontaneously in the air, and owing to the formation of smoke rings of silicon dioxide, it gives rise to phenomena which are quite similar to those which are seen in the case of hydrogen phosphide. Its behaviour, also, with respect to the dependence of the spontaneous ignition on the density, appears to be similar to that of hydrogen phosphide.

Whereas, therefore, in respect of the formula, silicon hydride and methane (p. 398) are to be regarded as similar compounds, they exhibit very great differences in their chemical properties. Similar differences are also found in the case of many other compounds of carbon and silicon of analogous composition.

Silicon Fluoride.—With fluorine also, silicon combines, yielding a compound of analogous composition, SiF_4, which at the ordinary temperature is a gas. This compound is very easily obtained by allowing hydrogen fluoride to act on silicon dioxide. Since it is decomposed by water, dehydrating agents must be added to destroy the action of the water which is formed in the process. This is most simply accomplished by treating a mixture of silicon dioxide and a saline fluorine compound (*e.g.* fluor-spar or calcium fluoride) with an excess of concentrated sulphuric acid. In place of silicon dioxide any silicate can be taken, since the hydrogen fluoride which is formed acts in the same way on all silicates.

* This reaction is of great importance analytically, since it gives us the means of bringing into solution, and thereby making accessible to analysis, the natural and artificial silicates, which otherwise show great resistance to chemical actions. For this purpose the silicates are covered with strong hydrofluoric acid and evaporated at a gentle heat. In this process a platinum dish must be used, as vessels of other material are attacked. The silicon fluoride passes off in proportion as it is formed, and the metals present are obtained as fluorides. Since

these would give bother in the further analysis, the evaporation is completed with the addition of sulphuric acid, the fluorides thereby passing into sulphates.

Silicon fluoride is a gas at the ordinary temperature, and passes, under the influence of pressure and cold, into a liquid which boils at about - 100°.

In contact with water, silicon fluoride also undergoes change; this, however, follows a somewhat different course from that in the case of the other halogen compounds. Instead of simply yielding hydrogen fluoride and silicic acid, an intermediate product, hydrofluosilicic acid, is formed according to the equation $3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4$.

Whereas the silicic acid separates out, the hydrofluosilicic acid dissolves in water and imparts to it an acid reaction. Where it is desired to obtain the latter, it is expedient to add so much hydrofluoric acid to the liquid that the silicic acid which separates out mostly passes into solution again—

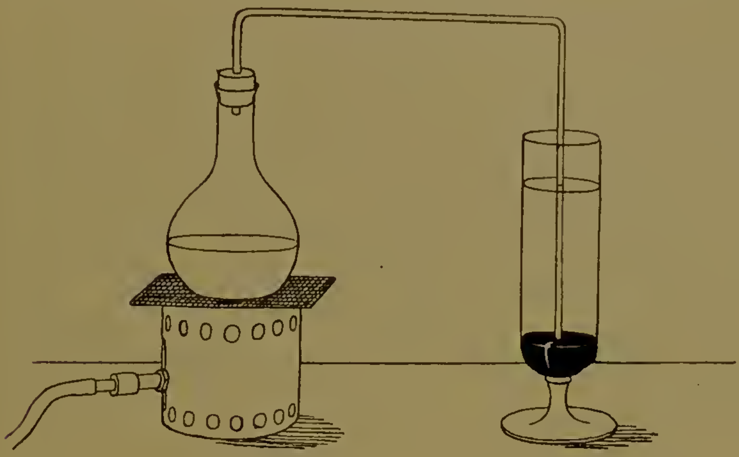


FIG. 103.

$$Si(OH)_4 + 6HF = H_2SiF_6 + 4H_2O.$$

The yield of acid is thereby increased and the troublesome filtration avoided.

* Since the silicic acid which is formed would soon stop up the delivery tube, it is necessary either to use an inverted funnel, through which the gas is allowed to pass into the water, or the delivery tube is made to open under the surface of a layer of mercury placed at the bottom of the vessel of water (Fig. 103).

Hydrofluosilicic acid is known only in aqueous solution. On evaporating such a solution, the acid passes off entirely; and if the evaporation is carried out in a vessel of glass or of porcelain, an etched spot is produced. This is due to the fact that the hydrofluosilicic acid decomposes into silicon fluoride and hydrofluoric acid in proportion as the solution loses water; the former escapes as a gas, and the hydrofluoric acid exerts its usual etching action. While, therefore, a solution of hydrofluosilicic acid does not itself attack glass, it does so if it is evaporated.

* On these chemical processes depends the etching of glass, which serves not only for the ornamentation of objects of daily use, but is still more important in the manufacture of scientific apparatus. If a glass surface is coated with wax, resin, or other substance capable of withstanding the action of hydrofluoric acid for some time, and this coating is then removed where necessary, the surface of the glass, on subsequent treatment with hydrofluoric acid, is attacked at all those parts which are uncovered, while the protected parts retain their polish.

* For example, in order to graduate a burette (p. 186), a suitable tube, on which the desired volume has been measured off, is coated with melted wax and the necessary strokes made in this coating by means of the dividing engine. After marking the figures also, concentrated hydrofluoric acid is brushed into the marks and again washed off after a few minutes. If the wax is then removed, the marks are found as hollowed lines in the glass, because the hydrofluoric acid dissolves a part of the glass wherever it comes into contact with it.

* The etching can be performed more cheaply, but not so conveniently, by first preparing hydrofluoric acid from a mixture of fluor-spar and sulphuric acid. The object is then placed over the mixture and the etching effected by means of the vapours of the acid which are evolved. This requires a considerably longer time, the length of which depends on the temperature.

* The etching produced by the vapours is dull, while that effected by the liquid acid is clear. This is due to the fact that in the first case only the gaseous silicon fluoride escapes, and the other constituents of the glass are left behind, while in the second case the glass is completely converted into soluble substances at the parts attacked. If to the aqueous acid substances are added which produce a precipitate on the glass, especially the alkali salts of hydrofluoric acid, a dull etching can also be obtained with the solution of the acid.

Hydrofluosilicic acid is a dibasic acid which forms many difficultly soluble salts. Thus the salts of the alkali metals, more especially, are almost insoluble in water, and barium silicofluoride is so to such a degree that it is used for the separation of barium in analysis. The acid is stable in acid solution; by excess of alkali it is, however, decomposed with formation of a silicate and a fluoride. To this is due the peculiar behaviour in the titration of this acid with alkali, *e.g.* with caustic soda. If this base is added to a solution of hydrofluosilicic acid coloured with litmus, a blue coloration, certainly, is produced when an amount of the alkali has been added corresponding to the hydrogen of the acid. After a few minutes, however, this colour again passes into red, and twice as much soda can be still added before the solution remains permanently blue. This is due to the occurrence of the following reaction:—

$$H_2SiF_6 + 6NaOH = 6NaF + Si(OH)_4 + 2H_2O.$$

Sodium fluoride and silicic acid are formed. Since the latter does not act on litmus, the blue coloration occurs when 6NaF are formed.

On this behaviour of the salts of hydrofluosilicic acid an analytical method for the determination of the alkali metals can be based, since these form difficultly soluble silicofluorides, which experience the above decomposition.

Carborundum.—Of the other compounds of silicon we shall still mention, on account of its technical importance, silicon carbide or carbon silicide. This is a greenish or black-coloured mass obtained by allowing carbon to act on silicon dioxide at the very high temperature of the electric furnace: $SiO_2 + 3C = SiC + 2CO$. The compound is distinguished by its very considerable hardness, and is therefore used in the arts as a grinding material. In chemical respects it is very resistant, since it is scarcely combustible, the silicon dioxide which is formed covering the surface with a coating which is impermeable for oxygen. It is slowly attacked when fused with caustic soda with access of air, sodium carbonate and silicate being formed.

Technically, the substance is called carborundum.

CHAPTER XVIII

BORON

General.—Among the non-metallic elements boron, occupies a rather isolated position, since the elements most nearly related to it must be sought for among the metals, namely among the earth metals. On account of the properties of the free element and of those of the compounds, it is, however, not expedient to give boron a place among the metals. It may best be classed along with silicon, from which it differs, however, in its typical compounds having a different composition.

Boron is a solid substance which is capable of existing in several different forms, one amorphous and at least one crystalline. Amorphous boron is obtained by passing the vapours of the chlorine compound over heated sodium, or, quite similarly to silicon, by igniting the oxygen compound with magnesium. After the removal of the admixtures, it forms a black powder of the density 2·5, which in many respects behaves similarly to charcoal, but is more easily oxidised; this occurs more especially by means of strongly oxidising solutions even at the room temperature.

By the fusion of boron trioxide (*vide infra*) with aluminium, crystallised boron is obtained, which, on account of its hardness, has been called "adamantine boron." It is not obtained quite pure in this way, but contains aluminium derived from its preparation. Since this metal is the element most nearly related to boron, the product is not to be looked upon as a compound, but as a mixture (possibly with a diamond-like form of aluminium isomorphous with boron, and not known by itself).

Boron containing carbon, and obtained from the two elements at a very high temperature, is of a similar character, and also possesses an adamantine hardness. This also ought most probably to be regarded as a mixture, and not as a chemical compound.

The two forms probably stand to one another in the relation that amorphous boron is unstable with respect to the crystalline, as white phosphorus is with respect to red. In this case, however, the velocity of transformation at temperatures below a red-heat is apparently immeasurably small.

The combining weight of boron is not known with great exactness; it may be put down at B = 11.

Boric Acid.—Of the compounds of boron, the most important are boron trioxide, B_2O_3, and the corresponding boric acid, which is formed from the trioxide by taking up the elements of water. The limiting compound which, on analogy with orthophosphoric acid, may be called orthoboric acid, is represented by the formula $B(OH)_3$. Although it is known in the free state, salts of the acid are not known with certainty. On the contrary, all known salts are derived from "condensed" acids.

In nature, boric acid occurs as *sassoline* in lustrous, generally somewhat yellowish coloured scales, which have a soft and smooth feeling and are soluble in water. Hot water dissolves a large quantity, cold water comparatively little. The crude boric acid can, therefore, be easily purified by recrystallisation. The purification is still more successfully effected by converting the boric acid into its sodium salt, *borax*, and decomposing this, after recrystallisation, in concentrated solution with an acid, *e.g.* hydrochloric acid. The boric acid then crystallises out as white scales.

Boric acid is a very weak acid, whose salts, on dissolution in water, are hydrolytically dissociated. The aqueous solution of the acid has a scarcely acid reaction, and conducts electricity only slightly better than pure water. Further, it cannot be titrated with caustic soda, since the alkaline reaction is gradually produced without a definite relation between acid and base being observed.

On being heated, boric acid loses water and passes into boron trioxide: $2H_3BO_3 = B_2O_3 + 3H_2O$. The anhydride formed melts to a glass-like mass, which is viscous and can be drawn into long threads. The fused substance dissolves various oxides of metals, and can, therefore, be used in soldering; for this purpose, however, the more readily fusible alkali salts of boric acid are employed.

Boric acid has fairly strong antiseptic action, and is therefore used in medicine and for pickling meat.

A very remarkable property of boric acid is that it is fairly readily volatile with steam, while its anhydride is highly resistant to heat. As a comparison with the other anhydrides, *e.g.* that of sulphuric acid, shows, this behaviour is unusual, for in by far the greater number of cases the anhydrides are much more readily volatile than the hydrates.

On this volatility of boric acid with steam depends the method of obtaining it. In the volcanic districts of Tuscany, vapours containing boric acid issue from the earth. By first passing these vapours into water and evaporating this water at a lower temperature, crystallised boric acid is obtained. The fact that all the boric acid does not thereby again pass off with the steam indicates that the ratio of boric acid to water vapour is at lower temperatures probably much smaller than at higher; as to this, however, nothing is known with certainty.

With the vapour of alcohol, boric acid is still more readily volatile. In this case it is the formation of a compound, an ester (p. 402), which effects the volatilisation. If the alcohol is set on fire, the flame is coloured green by the volatile ester of boric acid. This phenomenon can be used for the detection of boric acid; if this is in the form of a salt, it is only necessary to rub it up with sulphuric acid and to pour alcohol over the mixture, in order to obtain the reaction.

As in the case of phosphoric and silicic acids, there exist also in the case of boric acid various "condensed" acids, which are derived from orthoboric acid, $B(OH)_3$, by the loss of the elements of water. From orthoboric acid only the monobasic "metaboric acid" can be directly formed in this way; much greater diversity, however, is produced when *several* combining weights of boric acid together lose the elements of water. Of the many such forms possible, we shall mention only one, the dibasic tetraboric acid $H_2B_4O_7$, the formation of which is represented by the equation $4B(OH)_3 - 5H_2O = H_2B_4O_7$. This is the acid of the best known of all soluble borates, viz., *borax*, $Na_2B_4O_7$.

The boric acids, like the silicic acids, form soluble salts with the alkali metals, whereas all other metals yield difficultly soluble salts. When heated, the borates fuse to glass-like masses; in this state they dissolve the oxides of the heavy metals, which then often exhibit characteristic colours. These phenomena serve for the detection of such metals in analysis. Borates are also added to glass and enamel in order to impart to these particular properties, *e.g.* fusibility, small expansion with heat, and low power of refraction of light.

Other Compounds of Boron.—On heating amorphous boron, or a mixture of boron trioxide and charcoal, in a current of chlorine, there is obtained, as in the case of silicon, a readily volatile chlorine compound which condenses in the strongly cooled receiver to a liquid. In the pure state this is colourless, boils at 17°, and fumes strongly in moist air, since it undergoes decomposition with water to boric and hydrochloric acids: $BCl_3 + 3H_2O = H_3BO_3 + 3HCl$. From the vapour density, the molar weight of this compound is found to be 117, so that three combining weights of chlorine are contained in it. This is the reason why the combining weight of boron was not so chosen that its compounds could be formulated in accordance with those of silicon. Similar reasons are furnished by the other halogen compounds of boron which will presently be mentioned.

Boron trichloride can be regarded as the chloride of orthoboric acid, the three hydroxyls of which are replaced by chlorine. It may, therefore, be presumed that it is formed by the general method of preparation of the acid chlorides, by the action of phosphorus pentachloride on the acid. This is, as a matter of fact, the case, the reaction $B(OH)_3 + 3PCl_5 = BCl_3 + 3POCl_3 + 3HCl$ being possible.

With bromine, boron forms a tribromide, which is quite similar to the chloride.

Boron trifluoride is obtained as a colourless gas, which fumes strongly in the air and is quite similar to silicon fluoride, by warming boron trioxide with fluor-spar and concentrated sulphuric acid. In water it dissolves with great rise of temperature and separation of boric acid; in the solution there remains hydrofluoboric acid, HBF_4. This, it is true, has a different composition from hydrofluosilicic acid, but behaves quite similarly; for example, it also forms difficultly soluble salts with the alkali metals.

The reaction takes place according to the equation $4BF_3 + 3H_2O = 3HBF_4 + BO_3H_3$.

Hydrofluoboric acid is also obtained by adding boric acid or boron trioxide to aqueous hydrofluoric acid; these are quickly dissolved with considerable rise of temperature.

Of the other compounds of boron, boron nitride should be mentioned. It is formed by the direct combination of boron with nitrogen, and is generally formed in the preparation of boron if air be not excluded. It can also be obtained by igniting boron trioxide with charcoal in a current of nitrogen. When pure, it forms a white powder which phosphoresces in the flame, and when heated to a moderate temperature with water vapour is decomposed to boric acid and ammonia: $BN + 3H_2O = BO_3H_3 + NH_3$.

CHAPTER XIX

ARGON, HELIUM, AND CONGENERS

Argon.—It has already been mentioned (p. 314) that the nitrogen obtained from the air differs from the "artificial," *i.e.* obtained from chemical compounds, in having a somewhat greater density. This at first puzzling phenomenon was finally explained (Rayleigh and Ramsay, 1894) by the fact that in atmospheric nitrogen another gas is contained which resembles nitrogen in its disinclination to form chemical compounds, and indeed, in this respect, is considerably its superior.

By converting the nitrogen of the air into non-gaseous compounds, the other constituent, which has been called *argon*, can be obtained pure. For this purpose there may be employed, for example, the property of nitrogen of combining with oxygen under the influence of the electric discharge (p. 347). The nitrogen peroxide thus formed is absorbed by caustic soda, and by adding the necessary amount of oxygen the reaction can be continued till all the nitrogen is used up. The excess of oxygen can then be easily removed by means of heated copper or phosphorus (p. 316). The same end is attained by the use of certain metals, *e.g.* magnesium or lithium, which readily absorb nitrogen at a red-heat. A mixture of lime, magnesium, and some sodium has been found very suitable.

The residual gas is colourless, odourless, and tasteless, and has, in accordance with its density, the molar weight 40. It is, therefore, considerably more dense than nitrogen and oxygen. In the air it forms the 0·009 part by volume and the 0·012 part by weight, and the ratio of it to the other constituents of the air is not subject to any appreciable variations.

Since the gas does not form any compounds with other elements, no combining weight, properly speaking, can be assigned to it. On the basis of the law of Gay-Lussac (p. 139), it may, however, be assumed that if it did form any compounds, these must be formed with other gases in simple ratios by volume, and that, therefore, the normal weight 40, or some fraction of it, must be equal to the combining weight. What this fraction is, however, cannot *a priori* be stated.

A decision can be here arrived at by means of the relation which has been found to exist in the case of other gases between the composition and the *capacity for heat.* By capacity for heat there is understood the ratio of the heat communicated to a body to the rise of temperature produced. This ratio is evidently all the greater, the greater the amount of substance subjected to the experiment. If it is referred to one mole (p. 156) of the substance, this special capacity for heat is called the *molecular heat* or *molar heat* of the particular substance.

If the amount of heat be measured in Joules (p. 118), and the changes of temperature, as usual, in centigrade degrees, the following are the molecular heats of a number of gases :—

Oxygen	O_2	21	Carbon dioxide	CO_2	32
Nitrogen	N_2	20	Nitrous oxide	N_2O	33
Hydrogen	H_2	20	Water vapour	H_2O	28
Nitric oxide	NO	21	Phosphorous chloride	PCl_3	68
Carbon monoxide	CO	20	Chloroform	$CHCl_3$	69
Hydrogen chloride	HCl	20			

The smallest values of the molecular heats are, accordingly, 20, and are found in the case of those gases which contain two combining weights in the molar weight; it is thereby a matter of indifference whether the combined elements are like or different.

On determining the molecular heat of argon, however, the value 12 is obtained—a value, therefore, which is much smaller than that for all the gases given. This leads to the presumption that argon is still more simple in composition than these gases, *i.e.* that its molar and combining weights coincide, and that the formula of gaseous argon is given by the simple symbol A, and not A_2.

This presumption can be tested by analogy. From the chemical behaviour of *mercury*, the same conclusion has been drawn; mercury vapour must also have the formula Hg and not Hg_2, since the combining weight and the molar weight have both been found equal to 200. As a matter of fact, the determination of the molecular heat of mercury has yielded the value 13.

There is therefore sufficient reason for assuming the identity of the molar and combining weights of argon, and for ascribing to this element the combining weight 40, whereby the formula of gaseous argon becomes A.

For the rest, argon behaves similarly to the other gases. At $-187°$, under ordinary pressure, it becomes liquid.

If electric discharges are passed through rarefied argon, a spectrum of numerous lines is obtained. According to the pressure and the electrical conditions, three different spectra are obtained, the light in the tube appearing blue, red, or white.

Helium.—A considerable time ago the name helium was given to an unknown element, the presence of which in the sun's atmosphere had been concluded from the occurrence of a strong and constant line in the yellow-green of the spectrum which could not be referred to any known terrestrial element. In his investigations on the occurrence of argon in minerals, the same line was found by Ramsay, one of the discoverers of argon, in the gases which are evolved on the ignition of certain minerals, *e.g.* cleveite, and he established the fact that it was due to a gas similar to argon, and it accordingly received the name *helium*.

Helium is found in some rare minerals which contain the element uranium, and is obtained from these by heating. From any nitrogen which may be present, it can be freed in the same way as was given in the case of argon; from the argon which is sometimes also present, it must be separated by diffusion through a porous clay partition[1] (p. 93).

Helium is a very light gas, the molar weight of which is only 4; it is, therefore, only twice as heavy as hydrogen. Its critical temperature lies accordingly very low. For the rest, it shares the properties of argon, and has, more especially, the small molecular heat 12, so that its combining weight must be put equal to its molar weight. With this value, He = 4, helium is, next to hydrogen, the element with the smallest combining weight, so far as one can speak of such a thing in the case of an element which does not form any known compounds.

Further, in the residue from the evaporation of liquid atmospheric air, still a number of other gases have been discovered, which are characterised by their spectra and their density. They all likewise possess the small value of the molecular heat, and in all cases, therefore, the molar weight has been put equal to the combining weight. Their names are *neon* (Ne = 20), *krypton* (Kr = 81·8), and *xenon* (X = 128).

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[1] The separation is also effected by fractional distillation. On cooling the gases by means of liquid air, the argon condenses and the helium remains as a gas, dissolved, perhaps, in the liquid argon. On allowing the temperature to rise, the helium escapes first. By repeating the liquefaction and gasification, the gases can be separated.—Tr.

CHAPTER XX

POTASSIUM

General Remarks on the Chemistry of the Metals.—Although the number of the metallic elements is much greater than that of the non-metals, the chemistry of them is much simpler and comparatively less diverse. This is due to the fact that by far the largest number and the most important of the compounds of the metals are of a *saline* character. Now, we have seen generally, that the properties of the salts in aqueous solution are conditioned essentially by the properties of their ions. If, therefore, a metal, *e.g.* silver, forms only one kind of cation, the behaviour of all its salts in aqueous solution is known, if that of this particular cation is known; a knowledge of the anions, which have mostly been treated in the chemistry of the non-metals, is hereby supposed given.

So far, then, as the behaviour in aqueous solution is concerned, the chemistry of the metals is essentially given with the knowledge of the metal ions. In analytical chemistry we are concerned almost entirely with aqueous solutions, and to what we there learn it is generally sufficient to add a statement of the solubility relations of certain difficultly soluble salts, in order to obtain the foundation of analytical chemistry. For general chemistry, however, it is necessary to add a knowledge of the compounds in the solid state as well as of the non-saline or indifferent compounds which also exist in the case of the metals, whereby greater diversity is produced.

Some variety is, however, found among the ions themselves. Many metals form not only elementary ions with different properties, the differences between which are connected with different valency, but they are also capable of forming with other elements *complex* ions with special properties. New groups of substances are thereby formed, and in this direction inorganic chemistry is developing a very great diversity, which at the present time is by no means exhausted—in many cases indeed, its outlines are scarcely known.

In general, it must be said that every anion will be able to form a salt with every cation. By virtue of a general rule, most of the salts in dilute aqueous solution are extensively dissociated into their ions, so that the properties of these solutions differ but little from the sum of the properties of the ions. Where, therefore, specific properties, which do not correspond to this rule, are met with in salt solutions, it can be concluded with certainty that the dissociation of the salt present is small. From the comparatively great rarity of such exceptions, there follows, conversely, the great generality of the rule just stated.

In the following descriptions of the different metals, therefore, stress will be laid on the statement of the ions which can be formed from them, and the properties essential for their characterisation will be mentioned. In general, the methods employed for the detection and determination of the metals will be thereby given. To this there is added the chemistry of those solid compounds of the metals which are in any way important enough to find mention in this elementary work.

Potassium.—While the knowledge of some of the potassium compounds can be followed back almost to the most remote monuments of culture, the characterisation of the potassium compounds as derivatives of a special element was first effected towards the end of the eighteenth century by Marggraf. On account of the preparation of potassium carbonate from cream of tartar, which is deposited in the barrels in the fermentation of wine, that compound received the name of *vegetable* alkali, in contradistinction to *mineral* alkali, sodium carbonate or soda. Although potassium hydroxide or caustic potash could not be decomposed, it was long felt that it was no simple substance; but the actual proof that a metallic element formed the basis of the potassium compounds was first given in 1807 by H. Davy, who decomposed potassium hydroxide by an electric current derived from a voltaic battery, which had just then been invented.

After it had been obtained in this way, the method of preparing it by purely chemical means was soon discovered, a method which was for long the only one employed. The most important of these reactions is the heating of potassium carbonate with charcoal; carbon monoxide and metallic potassium are formed, the latter of which volatilises and is condensed under rock oil: $K_2CO_3 + 2C = 2K + 3CO$. Quite recently the electrical method of preparing it has been again adopted, since the necessary electrical energy can now be cheaply generated in any desired amount.

Potassium is a silver-white metal which melts at 62°, and which, even at the room temperature, is so soft that it can be kneaded and easily cut with a knife. At 720° it volatilises; the vapour is blue-green in colour. The colour can be rendered visible by heating the metal in a glass tube which is filled with a gas or vapour free from oxygen; the phenomenon, however, is visible only for a moment, since the potassium vapour quickly attacks the glass, which thereby becomes covered with a black coating of liberated silicon.

Potassium combines with very great readiness with oxygen, so that it decomposes almost all substances which contain that element. In the air, therefore, under the joint action of the water vapour, it immediately becomes tarnished, owing to the formation of a layer of hydroxide, and its metallic lustre can be observed only immediately after a fresh surface has been made. If it is enclosed in a tube which is exhausted or filled with hydrogen, and then fused, the metallic surface can thus be rendered visible and permanently preserved.

On account of this property, potassium must be kept in such a way that oxygen has no access to it. In large quantities it is preserved in a soldered tin; smaller quantities are kept under rock oil, since this liquid does not contain oxygen. It, however, absorbs gaseous oxygen, and the potassium kept under rock oil soon becomes covered with a grey-brown crust which, however, only slowly becomes thicker and protects the metal fairly well.

* It is very remarkable that in *dry* oxygen potassium is not (*i.e.* is only very slowly) oxidised, whereas the smallest amount of water immediately produces a rapid reaction. We have already (p. 396) met with examples of such catalytic acceleration of oxidation processes due to the presence of water. Such behaviour, however, in spite of its great generality, must not be regarded as universal, for instances of oxidation processes have been proved (*e.g.* the combination of nitric oxide with oxygen, p. 324) where the reaction takes place with undiminished velocity, even between the very carefully dried substances.

Concerning the determination of the combining weight of potassium, the essential points have already been given under chlorine (p. 222). It amounts to $K = 39{\cdot}14$.

Potassion.—Potassium can form only one kind of ion, viz., the monovalent potassion, $K^{\cdot}$. With metallic potassium the formation takes place with very great ease and energy. The chemical properties of the metal are essentially characterised by this fact, for it reacts on other substances in such a way that it passes into potassion, *i.e.* it forms a salt. Since, further, the passage of a solid salt into a dissolved one is in general accompanied by only a slight change of energy, it is of no essential importance for these reactions of potassium whether a dissolved or a solid salt is produced.

Isolated examples of such reactions have already been mentioned; the method of obtaining silicon and boron from their halogen compounds may be recalled. Since in these reactions the halogen compounds of potassium, *i.e.* salts of the metal, are formed, they come under the rule just stated.

The amount of heat which is liberated in the formation of potassion from the metal is very great; it is found, in accordance with the principles explained on p. 200, to be 259 *kj.*

If this quantity of heat is added to the heat of formation of an anion, the sum gives the heat of formation of the salt in dilute solution.

In order to obtain from this the heat of formation of the solid salt, it is only necessary to subtract the heat of solution, or to add its numerical value if solution takes place with absorption of heat, as is chiefly the case with the salts of potassium.

The aqueous solutions containing potassion are colourless if no other coloured compound is present, nor do they exhibit any other conspicuous property. For the higher animals, potassion in great concentration is a poison; in small quantities, however, it is an indispensable constituent of the organism. In the vertebrate animals it is contained, more especially, in the red blood corpuscles.

The *detection* of potassion in solution is accomplished by the aid of some acids which can form difficultly soluble potassium salts. For example, if a solution of perchloric acid be added to a solution containing potassion, there is precipitated, if the solution is not too dilute with respect to the latter, a crystalline precipitate of difficultly soluble potassium perchlorate. The same occurs on the addition of sodium perchlorate. In order to correctly understand the processes which are here met with, we shall first put forward a few general considerations.

Solubility.—By solubility there is understood the ratio of the amount of dissolved substance to that of the solvent in a saturated solution. The conceptions used here have, it is true, been already mentioned (p. 213); still, when several salts are present, the relations are rather more complicated, so that we shall consider them again connectedly.

If a solid substance and a liquid be brought together,[1] a certain amount of the solid substance passes into the liquid. This process does not go on indefinitely, but tends towards a certain point; for after a certain amount of the solid substance has passed into solution the process ceases, and the solution is "saturated."

A point of essential importance is that saturation is defined with respect to a definite solid substance *and changes when this solid substance changes.* The different polymorphic forms of a given substance, for example, have, therefore, *different* concentrations of saturation in the same solvent. In this connection, the general rule holds, that the solubility of the most stable form is always the smallest, and that the less stable forms are always more soluble in proportion as they are less stable (p. 259).

Solutions the concentration of which is smaller than that of the saturated solution are called *unsaturated;* those with a greater concentration, *supersaturated.* Both kinds of solution are stable *alone*, the unsaturated ones without limit, the supersaturated within certain limits, which depend on the nature of the substances and on the temperature. If, however, the unsaturated solution is brought into contact with the solid substance, the latter passes into solution until the concentration corresponding to saturation is established. In the case of the supersaturated solution, the solid substance separates in such amount that the same point is reached.

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[1] Solutions can be formed of substances in all three physical states, and can occur in all three states, so that there can be solid, liquid, and gaseous solutions of solid, liquid, and gaseous substances. Of these, however, the liquid solutions of solid substances are of such superior importance that we shall, in the first instance, confine the discussion to them.

* From this it follows, among other things, that a solution which is saturated in respect of an unstable form of a polymorphic substance, must be supersaturated in respect of the stable form of the same substance, and *vice versa.* Hence it follows, that when both substances are present together under a solvent, a state of equilibrium cannot exist, since the stable form must be deposited and the unstable be dissolved. Equilibrium is possible only when the unstable form has disappeared and been converted into the stable form. This is the explanation of the accelerating influence which every solvent exercises on such transformations.

If the degree of supersaturation is increased (*e.g.* by cooling down a solution of a substance whose solubility increases with the temperature), the solution passes from the state in which it does not deposit the substance spontaneously into that in which deposition occurs even when the solid phase is not present. The former state is called metastable, the latter unstable. The boundary between the two states is difficult to determine, although their pronounced features are easily demonstrated.

When small quantities of another substance are added to a saturated solution, the equilibrium changes, in general, only slightly, *i.e.* the solution remains nearly saturated.

In isolated cases there appear to be great deviations from this rule. Thus it has already been mentioned (p. 229) that the solubility of iodine in pure water is very small, but that large amounts of iodine can be dissolved in water containing iodidion. At the same place this was explained to the effect that in the solutions produced the iodine was not present as such, but was combined with iodidion to form the new ion I_3'. This, in turn, is partially dissociated into ordinary iodidion, I', and free iodine, I_2; and the latter is present in such quantity as corresponds to the solubility in pure water.

In the case of similar phenomena, therefore, which have the character of an increase of the solubility, the conclusion may always be drawn that the substance which has passed into solution has experienced a change, whereby its actual has become smaller than its apparent concentration.

Besides these cases of increased solubility, *diminutions* of the solubility have also been observed. These are found especially in the case of salts under quite definite conditions, and we shall now pass to a consideration of these.

Behaviour of Salts.—Salts also behave, in the first instance, in accordance with the laws of solubility, although in their case the process of solution is a more complicated one, since they do not pass unchanged into solution, but dissociate partially into ions. Experiment has, however, shown that for them also there exists a definite solubility, and that small additions of foreign substances have, in general, no great influence on the solubility.

An influence, however, is exerted in very considerable degree by foreign salts *which have an ion in common with the substance in question.*

If, for example, a saturated solution of the difficultly soluble potassium perchlorate (p. 218) be made, solutions of other salts, such as sodium chloride, magnesium sulphate, etc., can be added without any precipitation occurring. If, however, the solution of any potassium salt, *e.g.* potassium chloride, or of a perchlorate, *e.g.* perchloric acid or sodium perchlorate, be added, a distinct precipitate of potassium perchlorate is at once produced.

This phenomenon is universal; *every saturated solution of a salt becomes supersaturated in respect of this salt when the concentration of one of its ions in the solution is increased.* Whether or not this salt is *deposited*, depends on whether the solution formed is supersaturated to such an extent that the spontaneous formation of the solid phase occurs, or whether it is still in the metastable region (p. 117). These relationships are determined by the nature of the salt and the amount of the supersaturation.

Further, a supersaturated solution of potassium perchlorate is obtained when the solution of any potassium salt is brought together with that of a perchlorate, *i.e.* when potassion and perchloranion come together in the same solution. If the concentration of the two ions is not very small, the limits of the metastable state are immediately exceeded, and the solid substance separates out.

The conclusion may therefore be expressed as general that when the ions of a difficultly soluble salt meet in solution, that salt will separate out if its metastable limits are exceeded. For this separation both ions are essential; still, the experiments with the saturated solution of potassium perchlorate show that the two ions can mutually represent one another in their concentration. For if potassium perchlorate separates out from a solution which was saturated in respect of the pure salt, when the perchloranion is increased without increasing the potassion, there must be much less potassion contained in the resulting solution than in the first saturated solution. Similar reasoning holds for the second experiment. Whereas, therefore, the solution of a simple substance can be saturated only at a definite concentration of the solution, the saturation of the solution of a salt is possible with very different concentrations of its ions; but, when the concentration of one increases, that of the other must correspondingly decrease.

Theory of Solution Equilibrium.—The relationships just described follow as a necessary consequence from the law of mass action when the ions of the salts are regarded as independent constituents.

Let us consider the simplest case, that of a salt consisting of two monovalent ions, and let the concentration of the two ions be a and b, that of the undissociated part c; then, according to the law of mass action (p. 326), the equation

$$a \, . \, b = k \, . \, c$$

must hold for *every* solution of the salt.

In this equation k is the "equilibrium constant," which also depends on the temperature.

For the *saturated* solution, also, the same equation must hold. Let the corresponding values be called a_o, b_o, c_o; the equation then becomes

$$a_o \, . \, b_o = k \, . \, c_o.$$

On the right side of this equation are values which are constant at a given temperature. In the case where a salt is simply dissolved in water, the two ions are produced in the same concentration,[1] and, therefore, $a_o = b_o = \sqrt{kc_o}$ has a definite value. This value varies with the temperature, and therefore the solubility of pure salts is in complete accordance with the general laws developed above.

If, however, the two ions are present in different concentration, as when solutions of different salts are mixed, it is necessary for equilibrium that the *product* of the two concentrations a_ob_o shall assume a perfectly constant value. The greater the one concentration, therefore, the smaller must the other be in order that equilibrium be established. The product a_ob_o which corresponds to equilibrium is, therefore, called *solubility product*. In the case of difficultly soluble salts this is small; for easily soluble salts it is large. If the product of the ions present in a solution is greater than the solubility product of the corresponding salt, the solution is supersaturated in respect of this salt, and so much of it must separate out that in the remaining solution the value of the solubility product is reached.

If the product $a \, . \, b$ in a solution is smaller than the solubility product of the corresponding salt, the solution exerts a solvent action on the solid salt.

In these simple principles, the whole theory of precipitation and solution of saline precipitates is contained. As simple also as it appears, so diverse are its applications, and there will be frequent opportunity in the sequel of making use of the light which is thrown by this formula.

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[1] The concentration is to be measured here, as in all equations of equilibrium, in moles per litre. According to our system, it would be more correct to reckon moles per cc. (p. 325); since, however, very small numbers would be thereby obtained, it is more practical to employ the derived unit mole-litre.

* For example, at 15°, 15·4 gm. or 0·111 mole of potassium perchlorate dissolve in one litre. Since this dilute solution is almost entirely dissociated into ions, a_0 is also equal to 0·111 and $b_0 = 0·111$. Hence $a_0 b_0 = kc_0 = 0·0123$.

* Suppose, now, a solution given containing 0·5 mole potassion per litre, and let an equal volume of a solution of perchloric acid, containing one mole per litre, be added. The concentration of the potassion thereby sinks to 0·25, that of the perchloranion to 0·5; the product of the two is, therefore, 0·125. This value is a multiple of the "solubility product" 0·0123 found above for the equilibrium between potassium perchlorate and its aqueous solution. In order that equilibrium may be established, solid salt must separate out until the product of the remaining concentrations reaches the value 0·0123.

* When, now, the solid salt is deposited, both ions disappear in equal amounts. Let x be the amount of the solid salt measured in moles which will separate out, then $(a-x)(b-x) = 0·0123$. Since, by assumption, $a = 0·25$ and $b = 0·5$, it follows $x = 0·208$, *i.e.* the greater part of the potassion separates out, for only the amount $a - x = 0·042$, or a sixth of the original amount, remains in solution.

* The above relations become more complicated when we are no longer dealing with salts of monovalent ions. Since, however, the general relations are thereby not changed, but only the numerical laws, an exposition of the corresponding formulæ is, in the first instance, not required.

Other Reactions of Potassion.—The number of difficultly soluble potassium salts is limited, so that there are not many precipitation reactions for potassion. For analytical purposes, two acids especially are used, whose potassium salts are difficultly soluble, viz., tartaric and hydrochloroplatinic acids.

Tartaric acid is an organic compound of the formula $H_2C_4O_6H_4$; two hydrogens are written at the beginning to indicate that it is a dibasic acid. It forms, therefore, an acid and a normal potassium salt; of these, only the former is difficultly soluble. If a solution of tartaric acid be added to one containing potassion, the salt $KHC_4O_6H_4$ is precipitated as a crystalline powder.

Attention must, however, be paid to certain conditions which are essential to the success of the reaction.

In the first instance, tartaric acid is not a strong acid; its solutions contain for the most part undissociated tartaric acid along with the ions $H^{\cdot}$ and $HC_4O_6H_4'$ (hydrotartranion). It is the latter which determines the formation of the difficultly soluble precipitate on coming into contact with potassion; everything, therefore, which diminishes the concentration of the hydrotartranion will also impair the formation of the precipitate and make the reaction less sensitive.

Of such influences, hydrion comes especially into account. If tartaric acid is added to a solution containing potassion and also a large amount of hydrion, the latter unites with the hydrotartranion present to form undissociated tartaric acid, and the concentration of the remaining hydrotartranion can easily fall below the value necessary for precipitation. For the same reason, strong acids, *e.g.* hydrochloric acid, exercise a *solvent action* on the precipitate. They destroy in the saturated solution the hydrotartranion which is present, giving up their hydrogen for the formation of undissociated tartaric acid, and a further amount of potassium tartrate must therefore pass into solution to re-establish equilibrium.

Such an action can, evidently, occur only when the anion is that of a weak, *i.e.* slightly dissociated, acid, since the anion of a strong acid, which has no tendency to unite with hydrion, is not greatly changed by the presence of the latter. For this reason the solubility, for example, of potassium perchlorate and that of the potassium salt of chloroplatinic acid, which will be mentioned presently, is not appreciably altered by the presence of strong acids, *i.e.* of hydrion. We can therefore lay down the rule that *the difficultly soluble salts of* **weak** *acids are mostly soluble in* **strong** *acids, but not the difficulty soluble salts of strong acids.*

* When, therefore, it is desired to seek for potassion in an acid solution, the concentration of the hydrion must be made as small as possible. This can be done by carefully neutralising the solution with a base, *e.g.* caustic soda, with the help of litmus. The object can, however, be attained much more quickly by adding an indefinite amount of the sodium salt of a weak acid, *e.g.* of acetic acid. The anion of acetic acid contained in such a solution then unites with the greater part of the hydrion present to form undissociated acetic acid, and the residual amount of hydrion is reduced to a harmless amount. Of this method of weakening the action of the hydrion, very great use is made in chemistry, and we shall repeatedly have occasion to return to it.

* A further circumstance which has to be taken into account in testing for potassion with tartaric acid, is the length of time which solutions of the acid potassium tartrate remain supersaturated. Even when the solubility product has been rather considerably exceeded, no precipitate is formed at first, so that it appears as if no potassion were present. If the liquid is violently shaken, the salt is precipitated more quickly; still more certain action is produced by the addition of "nuclei," *i.e.* of exceedingly minute traces of the solid salt. A suitable preparation is obtained by powdering together a small quantity of the acid potassium tartrate with a hundred times its weight of a soluble substance, *e.g.* sodium nitrate. If, after the addition of tartaric acid, a quite small quantity of this mixture is added to the liquid to be tested for potassion and the whole well shaken, all possibility of supersaturation is done away with, and a precipitate is therefore sure to be formed if the solubility product was exceeded.

Another precipitant which is greatly used for potassion, especiall in quantitative determinations, is hydrochloroplatinic acid, frequentl but erroneously called platinic chloride. It is a compound of th composition H_2PtCl_6, and is, therefore, so far as the formula is concerned, similar to hydrofluosilicic acid, H_2SiF_6 (p. 425). A furth similarity exists in the fact that both yield difficultly soluble salts wit potassion; whereas, however, hydrofluosilicic acid also yields a simila salt with sodion, and cannot, therefore, be used for the separation the two elements; sodium platinochloride, in contrast with potassiu platinochloride, is very readily soluble in water and alcohol.

If, therefore, hydrochloroplatinic acid is added to a solution containing potassion, the solubility product is exceeded even when th concentration of the former is very small, and the salt K_2PtCl_6 sep rates out as a yellow precipitate, which microscopic examination show to consist of regular, transparent octahedra. The reaction can b rendered much more sensitive by the addition of alcohol, since th salt is much more difficultly soluble in alcohol than in water.

Since hydrochloroplatinic acid is a strongly dissociated acid of th same order as hydrochloric acid, the presence or absence of hydrio is of no account, although it has an influence in the case of tartari acid.

Potassium Hydroxide.—When potassium is brought into contact with water, violent action takes place; hydrogen is evolved, an usually takes fire in consequence of the high temperature produced and the potassium is converted into potassium hydroxide $2H_2O + 2K$ $= 2KOH + H_2$.

The flame of the burning hydrogen has a reddish-violet colour this is due to potassium, which imparts this colour to flames in whic it is present. The potassium hydroxide which is formed does not, a a rule, dissolve immediately in water, but forms a fused incandescen ball which, on account of its high temperature, is not wetted by th water; when all the potassium has been used up and the flame is extinguished, the ball still floats some time on the water until its temperature has so far sunk that wetting occurs. It then dissolves with s great an evolution of heat that an explosive formation of steam occurs and small particles of the hot mass are projected in all directions Since potassium hydroxide has a strongly corrosive action, thes particles can do considerable damage, and care must be taken by timely covering of the vessel that they do not become scattered.

The action of potassium on water is much more moderate whe the metal is dissolved in mercury. This solution is called potassiu *amalgam*, amalgam being the general name for those metallic alloy which contain mercury. In the laboratory it is prepared by dissolvin metallic potassium in mercury; considerable amounts of heat are se free in the process.

On the large scale, potassium hydroxide is prepared by the actio f potassium amalgam on water, the necessary amalgam being prepared y an electrical method. If a solution of potassium chloride is lectrolysed, chloridion goes to the anode and potassion to the cathode. f the latter is formed of mercury, the potassium, after losing its lectric charge, dissolves in it and forms potassium amalgam (p. 196). his acts in another part of the apparatus on water, and is converted nto potassium hydroxide with evolution of hydrogen, in accordance ith the equation given above; the mercury, free from potassium, gain passes back to the cathodic space.

A solution of potassium hydroxide can also be obtained electroytically by using an anode of some other metal, *e.g.* iron. In this ase no potassium at all separates out, but only hydrogen is evolved, ith the simultaneous formation of potassium hydroxide. It has lready been remarked (p. 195) that in this process we may look upon otassium as being first formed, and then reacting secondarily with ater to give potassium hydroxide and hydrogen. Another, and peraps more correct view, is to regard the hydrogen as primary by ssuming that the hydrion, which is present in small amount in the ater, is discharged and forms hydrogen. The corresponding amount f hydroxidion remains in solution, and forms potassium hydroxide ith the potassion. In proportion as hydrion is thereby used up, fresh quantity is formed from the water. Both ways of viewing he process lead practically to the same result, and the considerations hich cause the one or the other view to be regarded as the better ill not be put forward here, since at this point nothing of an essential haracter depends on them.

* The method just given appears simpler than the previously escribed mercury method. To it, however, there attaches the very reat difficulty that the cathodic space, in which the caustic potash is ormed, must be very carefully separated from the anodic space, in hich the chlorine is evolved, since, otherwise, the two substances ould act on one another. At the same time it is required that the lectric current shall pass through unimpeded. The porous septa of archment paper, animal bladder, or clay which are usually employed, o not resist the simultaneous action of chlorine and caustic potash, nd the use of the method is dependent on the satisfactory solution of he "diaphragm question."

Further, potassium hydroxide is obtained by a chemical method y decomposing potassium carbonate in dilute solution with calcium ydroxide. Since calcium is a divalent metal, the latter compound as the formula $Ca(OH)_2$, and the reaction takes place in accordance ith the equation $K_2CO_3 + Ca(OH)_2 = CaCO_3 + 2KOH$. The following ay serve as an explanation of the process.

Calcium hydroxide is a slightly soluble substance, since one litre of ater dissolves less than 2 gms. of it; calcium carbonate is a very ifficultly soluble salt, the solubility of which is at least a hundred times as small as that of calcium hydroxide; potassium carbonate an potassium hydroxide, on the other hand, are readily soluble salts. a solution of potassium carbonate is brought together with soli calcium hydroxide, a small quantity of the latter, in amount corr sponding to the above stated solubility, dissolves. The solution the contains the ions $Ca^{\cdot\cdot}$, OH', $K^{\cdot}$, and CO_3''. Of the four possible sal which can be formed from them, calcium carbonate has by far th smallest solubility product, and since the values of the concentratio of $Ca^{\cdot\cdot}$ and CO_3'' in the solution yield a much larger product, it follow that calcium carbonate must separate out in the solid form.

When the concentration of the calcion has thereby become smalle fresh calcium hydroxide must pass into solution; the calcion fro this is in turn precipitated by the carbanion, and if a sufficient amour of calcium hydroxide is present, the process goes on until the co centration of the carbanion has fallen to the small value which corr sponds to the solubility of calcium carbonate. Besides these ver small amounts of calcion and carbanion, only potassion and hydroxi ion remain in the solution, *i.e.* potassium hydroxide has been formed.

* It must here be remembered that the solubility of the calciu hydroxide becomes smaller and smaller by reason of the increase i the concentration of the hydroxidion during this process, *i.e.* a decrea ingly small concentration of calcion suffices to give the solubility pr duct of calcium hydroxide. The amount of carbanion finally remai ing in solution is correspondingly greater than in the case of a pur solution of calcium carbonate. This circumstance becomes more pr minent, the more concentrated the solution becomes in respect c hydroxyl. For this reason, the process must be carried out in dilut solution (at most 8 per cent) in order that the decomposition may b sufficiently complete.

As can be seen, this method is an application of the genera principle that from a solution containing different ions, that com pound of these, or that salt, separates out whose solubility product i exceeded.

In practice, the above process is carried out at the temperature c boiling. In the cold, the calcium carbonate, indeed, separates out in much more soluble, amorphous form, which only slowly passes into more stable and less soluble form; at the temperature of boiling however, the transformation takes place very quickly. An excess o calcium hydroxide is used, and the mixture is boiled until no bubble of carbon dioxide are formed, when a sample of the clear, settle liquid is supersaturated with an acid. Since the hot solution attack glass and porcelain, vessels of iron, which are resistant to a solution o caustic potash, are employed.

By evaporating the solution, solid potassium hydroxide, KOH usually called caustic potash, is obtained. The peculiarity is her found that solid substance is not deposited at a definite concentra tion on evaporating the boiling liquid, as is the case with other salts; but the solution always remains liquid, while its boiling point rises, and finally it forms fused potassium hydroxide.

* It must not be concluded from this that solid potassium hydroxide is soluble in water in all proportions: such a relation never occurs between a solid and a liquid substance. It can, however, be concluded that *there is no saturated solution of potassium hydroxide in water whose vapour pressure at the temperature of saturation is as much as one atmosphere.*

* At all temperatures between the freezing point of a saturated solution of caustic potash and the melting point of the anhydrous caustic potash, there can be saturated solutions of caustic potash in water, *i.e.* liquids which consist of caustic potash and water and are in equilibrium with solid potash. At the equilibrium or saturation temperature, each of these liquids has a definite vapour pressure. This approaches zero at both ends of the chain of physical states referred to above. On the one hand, at a low temperature, the vapour pressure of the saturated solution is, of course, very small; on the other hand, the first portions of water are held so firmly by the fused potash that even the vapour pressure of this liquid commences with very low values, in spite of the high temperature. Between these two extremes, the values of the vapour pressure must be such that they reach a maximum at an intermediate point. In the case of most salts, this maximum is greater than one atmosphere; in the case of caustic potash, it is less.

* If, therefore, the solution of caustic potash be boiled down under a sufficiently low pressure, the solid substance will be seen to be deposited, just as is the case with most other substances when the concentration is carried out under the ordinary atmospheric pressure.

In Fig. 104, the line *kk* represents, diagrammatically, the vapour pressure of the saturated solutions of caustic potash as a function of the composition of the saturated solution, the total amount of potash plus water in the solution being put equal to unity; *aa* represents the atmospheric pressure, and *ss* the vapour pressure curve of any other salt in the case of which the deposition of the solid substance is exhibited on concentration under atmospheric pressure. The curves are drawn only diagrammatically, and do not represent actual measurements; none such have as yet been made in the case of caustic potash.

Chemical Properties of Potassium Hydroxide.—Potassium hydroxide or caustic potash, is the type of a strong base. In aqueous solution it is very extensively dissociated into its ions, and the properties of hydroxidion are, therefore, very strongly developed. Even in very dilute solution it colours litmus blue and phenolphthalein red. Somewhat stronger solutions have a soapy feeling, because they dissolve the skin of the fingers and convert it into a slimy mass; they exhibit a similar solvent action on fats, horn, hair, and like animal substances. Acids of all kinds are neutralised, *i.e.* converted into potassium salts, and neutral salts containing other metals are mostly decomposed in such a way that potassium salts are formed and the metals are deposited as hydroxides.

Since the last reaction is largely made use of in analysis and for technical purposes, a short discussion of it will be given. If a solution of caustic potash is added to the solution of a salt the metal of which forms a difficultly soluble hydroxide, this hydroxide will be precipitated, because so much hydroxidion is introduced into the solution by means of the potash that the solubility product of the hydroxide in question is greatly exceeded. Since, now, the hydroxides of almost all the metals except the alkali metals are less soluble than potassium hydroxide, their salts are all decomposed in the above manner by potash solution.

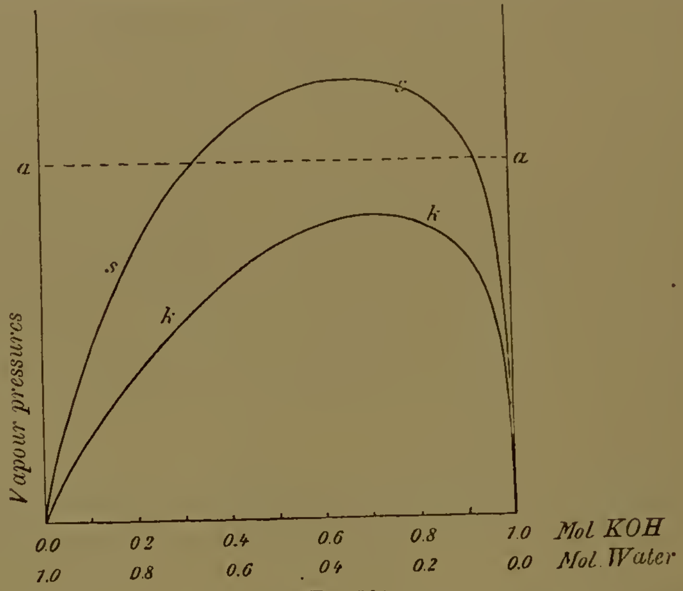

FIG. 104.

* Thus, solutions of zinc salts give a white precipitate; of zinc hydroxide with caustic potash, solutions of nickel salts, a green; and copper salts a blue precipitate of hydroxide. Ammonium salts on being heated after the addition of caustic potash, evolve ammonia gas, which can be detected by its smell and by the fumes which it gives with hydrochloric acid (p. 338), because the ammonium undergoes transformation with the hydroxyl to water and ammonia.

All these reactions are due to hydroxidion and not to potassion, for the same reactions are given when the latter is replaced by sodion or the ion of any other alkali metal. What has just been said is, therefore, not a description of caustic potash in particular, but of the strongly dissociated hydroxides in general.

The special properties of potassion have already been given (p. 437).

Potassium Chloride.—The most widely distributed salt of potassium, and the one which is most important technically, is potassium chloride, KCl. It occurs naturally in regular crystals as *sylvine;* it is found, however, in much larger quantities, united with magnesium chloride, as *carnallite.* The latter mineral will be described under magnesium, as will also the method of obtaining potassium chloride from it.

Potassium chloride is a colourless salt which is readily soluble in water, and which fuses only at a fairly high temperature (730°) to a colourless liquid which, on solidifying, forms the same regular crystals as are obtained from the aqueous solution. The solubility of potassium chloride in water increases almost proportionally with the temperature: at 0°, 100 parts of water dissolve 28 parts of the salt; at 100°, 57 parts (p. 215).

The solutions exhibit the reactions of the ions of the salt.

Being the cheapest potassium salt, potassium chloride is used for preparing numerous other potassium salts and as a fertiliser. Potassium is an essential constituent of plants; the quantity of this element required by the different plants is, however, different. More especially in the case of the sugar beet is a large amount of potassium necessary. Now, the normal soil contains rather considerable quantities of potassium, chiefly, it is true, in the form of compound silicates. On account of the slight tendency to decompose, these silicates are, however, available in such small amount that where there is a long continued occupation of the soil by plants which take up large quantities of potassium, a compensation by soluble potassium salts is necessary. This purpose is served by the manures containing potassium.

These are obtained from naturally occurring mineral beds which extend widely through North and Middle Germany; they have been worked with most success at Stassfurt. There, are found, lying on an enormous layer of common salt (sodium chloride), extensive beds of potash minerals (abraumsalts), from the nature of which it is probable that we are here dealing with the residues of the evaporation of a former sea.

Potassium Bromide, KBr, is a white salt which crystallises in regular forms, is readily soluble in water, and is generally employed for all purposes for which bromidion is used. Large amounts of it are used in photography for the preparation of silver bromide; it is also used in medicine.

Potassium bromide is chiefly obtained from bromine by dissolving this in caustic potash. The resulting mixture of bromide and bromate p. 228) can be easily separated by crystallisation into its components, f use can be made of the bromate. If the bromate is not desired, he salt mixture is heated with charcoal, the bromate being thereby converted into bromide: $2KBrO_3 + 3C = 2KBr + 3CO_2$.

Potassium Iodide, KI, is used, similarly to potassium bromide in all cases where iodidion has to be applied, and more especially fo the preparation of other iodides. It is a white salt, which crystallise in anhydrous cubes, and is still more readily soluble in water tha potassium bromide; it readily becomes coloured yellow from th separation of free iodine (due to the carbonic acid and the oxyge of the air).

Potassium iodide is prepared from iodine by converting this int iodide of iron by means of water and iron, and precipitating thi with a solution of caustic potash. Ferric hydroxide is deposited an potassium iodide remains in the solution and can be obtained b evaporation.

Potassium Fluoride, KF, is obtained as a white salt, readil soluble in water, by evaporating a solution of caustic potash whic has been neutralised with hydrofluoric acid. Its aqueous solutio attacks glass, and the preparation must, therefore, be carried out i vessels of platinum.

Potassium fluoride is distinguished from the other halogen com pounds of potassium in many respects. At ordinary temperatures, i crystallises with water of crystallisation, forming crystals of th composition $KF + 2H_2O$, while the others are anhydrous. Further it is capable of combining with an excess of hydrofluoric acid to forn an acid salt.

If to the solution as much hydrofluoric acid is added as wa required for neutralisation, and the solution is evaporated, ther crystallises out a salt of the composition HKF_2, which, on bein strongly heated, decomposes into neutral potassium fluoride an anhydrous hydrofluoric acid: $HKF_2 = KF + HF$. The hydrofluori acid behaves as if it were a dibasic acid of the composition H_2F_2.

* Since such a composition cannot be formulated in accordanc with the ordinary theory of valency, the compound has been describe as a so-called molecular compound, the latter being regarded a different from the compounds in the narrower sense. No differenc between the two kinds of compounds can, however, be detecte experimentally, and it must just be laid down as a fact that hydr fluoric acid can also act as a dibasic acid. The relations actuall existing are not yet accurately known, but it is probable that i the comparatively concentrated solutions of hydrofluoric acid. th compound HF exists as well as H_2F_2 along with their ions. solution of the acid potassium salt would, accordingly, contain th ions $K^{\cdot}$ and HF_2' along with the ions $2F'$ and $H^{\cdot}$, as the dissociatio products of the ion HF_2'.

Potassium Chlorate, $KClO_3$, is a salt which crystallises i anhydrous monoclinic laminæ, the solubility of which in water i small at low temperatures, but very considerable at high. If th solubility is represented as ordinates and the temperature as absciss

(Fig. 72, p. 215), a curve is obtained which is convex on the under side, *i.e.* the increase of the solubility is not proportional to the temperature, but is more rapid.

The formation of potassium chlorate by passing chlorine into a solution of caustic potash, does not differ from that of sodium chlorate (p. 211). Since in this process only a sixth of the potassium is converted into chlorate, the potash is replaced by the cheaper calcium hydroxide, which, in a perfectly similar manner, yields calcium chloride and calcium chlorate. To the solution is added potassium chloride in amount corresponding to the quantity of calcium chlorate; on cooling down the liquid, the product of the concentrations of potassion and chloranion is considerably greater than the solubility product of potassium chlorate, and this salt, therefore, is deposited.

The chlorine required for the reaction is now no longer prepared by a chemical method, as formerly, but *electrolytically.* As was shown on p. 445, hydrogen and caustic potash are formed at the cathode and chlorine at the anode, when a solution of potassium chloride is electrolysed. While it is of essential importance to keep these two products separate where it is a question of obtaining the caustic potash, they must be allowed to act on one another when the object is to prepare potassium chlorate, and, in contrast with the former case, it is especially advantageous to effect the mixing of the two substances as quickly and as completely as possible. In places, such as Switzerland and Norway, where electrical energy can be obtained cheaply by means of water power, the whole amount of chlorates required is now prepared in such a manner.

Since in this reaction all the potassium chloride can be finally converted into chlorate and only hydrogen is formed as by-product, the chemical process can be summarised in the equation $KCl + 3H_2O = KClO_3 + 3H_2$. Such a process does not take place spontaneously, since the substances on the right side of the equation contain much more energy (more both of total energy and of free energy) than those on the left from which they are formed. To make such a process possible, therefore, free energy must be communicated, and this is done in the form of the electric current.

* The action of the latter consists in converting the ions which are present into neutral substances (or, *vice versa*, neutral substances into ions) at the electrodes. Since changes of energy always accompany this transformation, two different cases may arise. In the first place, the sum of the transformations may be accompanied by an *elimination* of free energy; the chemical energy can then be utilised for obtaining electrical energy in the form of a current. This occurs in the galvanic cells, in which chemical energy is transformed into electrical; these will be discussed later. In the second case, the substances which are formed contain *more* free energy that the original ones; in this case electrical energy must be expended in order to render the reaction

possible, and electrical energy is transformed into chemical. This is the case in the preparation of potassium chlorate just described.

Potassium chlorate is used chiefly on account of the large amount of oxygen which it contains, and of the ease with which it gives this up. The use of this salt for obtaining free oxygen in the laboratory has already been mentioned. It is further used in pyrotechnics and in the preparation of explosive mixtures. Such mixtures are obtained when this salt is mixed with combustible substances; according to the nature of the latter, the mixtures burn with greater or less rapidity, or are explosive.

* Thus, very rapidly burning mixtures, which can be ignited by percussion or by friction, are obtained by mixing potassium chlorate with sulphur or sulphur compounds of the metals. A mixture of equal parts of potassium chlorate and antimony sulphide can be made to undergo sudden combustion with violent detonation when placed on a hard support and struck with a hammer. It explodes much more readily with friction, so that it must be prepared and handled with care. It is the most essential constituent in the heads of the so-called Swedish safety matches.

Large quantities of potassium chlorate are also used in dye-works. There are certain dyes (aniline black) which are formed on the fibre by the oxidation of other substances which are soluble. In those cases where the oxygen of the air is not sufficient, chlorates are employed. At the ordinary temperature these, certainly, do not give up their oxygen quickly, but by the addition of catalytic accelerators (copper or vanadium salts) velocities are attained which can be utilised in practice.

When hydrochloric acid is poured over potassium chlorate, large quantities of chlorine are evolved: $KClO_3 + 6HCl = KCl + 3H_2O + 3Cl_2$. This mixture is, therefore, often used in analysis in place of *aqua regia*, especially for the oxidation of the metallic sulphides. In carrying out this operation, hydrochloric acid is poured over the substances and potassium chlorate added in small quantities in the cold.

* The same mixture is used for the oxidation of organic substances in testing foods or parts of the organism for mineral poisons. In this case the oxygen of the potassium chlorate acts directly as oxidising agent.

All these reactions depend on the transformation of chloranion into chloridion, with evolution of oxygen: $ClO_3' = Cl' + 3O$. They are, therefore, also given by the chlorates of the other metals. That it is potassium chlorate which is almost exclusively used for this purpose is due to the fact that it is, of all the chlorates, the one which has been longest known and is the easiest to prepare pure. In many cases, however, its slight solubility at medium temperatures is a disadvantage; it is then replaced by the much more readily soluble sodium chlorate (which see).

The evolution of oxygen from fused potassium chlorate is greatly accelerated by the presence of foreign substances which do not take part in the reaction. In this respect, ferric oxide is the most efficient; if finely powdered potassium chlorate is mixed with a fourth of its weight of ferric oxide and the mixture heated at one point, it becomes incandescent, and decomposes with almost explosive violence. A similar though feebler action is exerted by manganese dioxide, and this is therefore chiefly used to facilitate the decomposition of the chlorate (p. 62).

The action is partly due to the fact that the fine powder of the substances added facilitates the evolution of gas owing to the presence of air bubbles, as happens in the case of supersaturated gas solutions. For the decomposition of potassium chlorate into potassium chloride and oxygen is not a process of dissociation which leads to a measurable chemical equilibrium, but a process which takes place only in one direction, such as, *e.g.* the combustion of charcoal in oxygen. The reaction, also, practically cannot be reversed; no measurable amount of potassium chlorate is formed by heating potassium chloride in oxygen.

Potassium chlorate has, therefore, to be regarded as an unstable compound, whose existence depends on the fact that the decomposition which it undergoes takes place so slowly as to be inappreciable by the ordinary means of detection. Even at the temperature of fusion, the velocity of decomposition is not considerable when the substance is pure, but is accelerated by the removal of one of the products of decomposition, oxygen. This is accomplished by the presence of porous powders in the manner just stated. The velocity is further accelerated catalytically by the substances mentioned. This follows from the fact that powders of approximately the same degree of fineness and enclosing the same amount of air exert, at the same temperature, a very different action on the fused chlorate; the one causes only a moderate, the other a violent decomposition.

The latter is all the more dangerous the larger the amount of salt decomposed at one time. From the thermochemical measurements it is found that in the decomposition of potassium chlorate into potassium chloride and oxygen, 34 *kj* are evolved. From this it follows that the salt undergoing decomposition must rise in temperature; the decomposition is, however, thereby accelerated. If, by using comparatively large quantities, the dissipation of the heat is made small, the temperature rises so high that complete decomposition occurs in a very short time. These are, however, the phenomena of explosion.

* The catalytic action of the substances named can be demonstrated by carefully fusing pure potassium chlorate and waiting till the evolution of gas, which usually occurs, has ceased. If into the quietly flowing melt, after removing it from the flame, a little manganese dioxide is thrown, the liquid mass immediately froths violently, although the temperature is lowered by the cold powder.

Potassium Perchlorate, $KClO_4$, is formed when potassium chlorate is carefully heated (p. 218), and can, by reason of its small solubility, be easily separated from the potassium chloride which is formed at the same time. It is, it is true, more rich in oxygen than potassium chlorate, but it is only slightly employed for purposes of oxidation, because it gives up its oxygen much more slowly than the latter. On account of its small solubility, which can be further considerably diminished by addition of alcohol, it is occasionally used for the separation of potassion in analysis. For this purpose a sufficient quantity of perchloric acid is added to the solution, and so much anhydrous alcohol that the solution contains at least 70 per cent of the latter. Since of all the salts of perchloric acid, potassium perchlorate is the most easily prepared, it is used for the preparation of that acid by distillation with sulphuric acid (p. 218).

Potassium Bromate, $KBrO_3$. The formation of this salt, along with potassium bromide, by the interaction of caustic potash and bromine, has already been mentioned (p. 228). It is the salt in which bromanion is most readily accessible, but there are only few cases in which this finds application.

Potassium bromate is more difficultly soluble in water than the chlorate, with which it is isomorphous, and, like most of the potassium salts, it crystallises anhydrous. On being heated, it readily decomposes into potassium bromide and oxygen; as a rule, some bromine is thereby set free.

Potassium Iodate, KIO_3, is a slightly soluble salt which can be obtained in various ways. On dissolving iodine in caustic potash, potassium hypoiodite is first of all formed along with potassium iodide; the former, however, passes quickly (much more quickly than the hypochlorite) into potassium iodate and potassium iodide, which can easily be separated from one another on account of the great difference in solubility. Potassium iodate is further formed by exposing potassium iodide to oxidising actions, *e.g.* in a current of chlorine.

It can be obtained still more easily by carefully heating a finely powdered mixture of potassium chlorate and potassium iodide to a temperature at which the potassium chlorate just begins to decompose. There then occurs the reaction $KClO_3 + KI = KIO_3 + KCl$, and the two salts can be readily separated from the fused mixture by crystallisation.

Finally, when a little nitric acid is added to the solution, iodine reacts with potassium chlorate and yields potassium iodate, chlorine being evolved: $2KClO_3 + I_2 = 2KIO_3 + Cl_2$.

Potassium iodate crystallises anhydrous from neutral solutions. If these are acidified, acid potassium iodate, of the formula KHI_2O_6, is obtained on crystallisation. This is another example of the fact that monobasic acids can yield acid salts like dibasic acids.

* Acid potassium iodate is a substance which can be used in many

ways in volumetric analysis, since it crystallises anhydrous and can be easily weighed. On the one hand, by dissolving weighed quantities of it, solutions of a definite *acid* titre are obtained; it can, therefore, be used as the starting substance for the determination of acids and bases. On the other hand, with excess of potassium iodide and acid, it gives an amount of free iodine which can be calculated from the equation $KHI_2O_6 + 10KI + 11HCl = 11KCl + 6H_2O + 6I_2$, so that it can also be used as the basis for iodometry (p. 297). However, it is not quite easy to prepare a salt of constant composition, for besides the salt just mentioned, there is a salt $KH_2I_3O_9$, which separates out from more strongly acid solutions.

Potassium Carbonate, K_2CO_3, was, before the discovery of the German potash beds, the salt of potassium which was available in greatest abundance, and was therefore the most important. It is called *potashes* because it was obtained from the ash of wood and other parts of plants. In plants the potassium salts of organic acids occur; when the plants are burned, the carbon of the acids passes into carbon dioxide and the potassium remains in the ash in the form of the carbonate.

To obtain it from this, the ash is extracted with water; the soluble salts, of which the chief is potassium carbonate, are dissolved, and the insoluble constituents remain behind. To obtain the salt itself, the solution must be evaporated. The expenditure necessary for this is all the greater the greater the quantity of water, relative to the amount of salt, which has to be removed; it is, therefore, of importance that a solution should be prepared which is as concentrated as possible. On the other hand, it is just as important to extract the salt as completely as possible from the ash, for which purpose repeated extraction with fresh water is necessary.

The fulfilment of these two apparently opposed demands becomes possible by means of the principle of *counter currents*, already mentioned. Let there be given a series of vessels with ashes, A, B, C, . . . If, now, A is extracted with a certain quantity of water, the solution, on the one hand, is by no means saturated with potassium carbonate, and, on the other hand, a large amount of the salt remains behind with the ashes, since all the solution cannot be removed. For the extraction of B there is used, not pure water but the solution from A, and A is extracted with a fresh portion of pure water. By this means a much more concentrated solution is obtained from B and a much smaller residue remains in A. The solution from B goes to C and dissolves more salt; the solution from A is used for the extraction of the residues in B, and by a third quantity of pure water the salt still present in A can be almost completely removed.

If this process is continued systematically, the solvent water moves in one direction and the ashes to be extracted in the opposite direction; by this means almost completely lixiviated ash is exposed to the action of fresh water, and the almost saturated solution acts on fresh ash, the result of which is, on the one hand, a well lixiviated residue, and, on the other, an almost saturated solution. By means of this arrangement, on the principle of counter-currents, no more water is used than is necessary to dissolve the salt, and, on the other hand, the soluble matter is removed from the residues as completely as is desired.

The same process, which has, for the sake of clearness, been here described as being carried out in different vessels, can be so arranged as to go on continuously. The same object is attained if we imagine the ash to be slowly moved upwards by means of some mechanical contrivance, while at the same time water trickles from above downwards.

Besides occurring in the ash of plants (the ash of bituminous and of brown coal contains almost no soluble substances), potassium carbonate is also found abundantly in the residues which are left in working up the sugar beet (molasses charcoal); further, not inconsiderable quantities of organic potassium salts are obtained in the water in which raw sheep's wool has been washed.

The potassium carbonate obtained from the above sources is of no great purity. To obtain a pure salt, it is well to prepare the much less soluble potassium bicarbonate (*vide infra*) and to convert this into the carbonate by heating.

Potassium carbonate is also prepared in large quantities from potassium chloride. For this purpose, the electrolytic decomposition may be employed whereby potassium hydroxide is formed (p. 445); on passing carbon dioxide into the liquid around the cathode, potassium carbonate (or bicarbonate) is, of course, obtained in place of the hydroxide. It can also be prepared from potassium chloride by a process exactly similar to that used for preparing sodium carbonate from common salt, and which will be described under sodium. Finally, potassium carbonate can be obtained from potassium chloride by way of a double salt with magnesium carbonate; the chemical reactions occurring here will be given under magnesium.

Potassium carbonate is a white salt which is very soluble in water. Since the vapour pressure of the solution saturated at the ordinary temperature is considerably smaller than the average vapour pressure of the water in the air, the salt deliquesces in the air to a thickish liquid which, after standing some time, again becomes solid. This is due to the fact that the salt absorbs carbon dioxide from the air and slowly passes into potassium bicarbonate (*vide infra*). By carefully evaporating the aqueous solution at a low temperature, hydrated crystals of the composition $2K_2CO_3 + 3H_2O$ are obtained.

The aqueous solution of potassium carbonate has a fairly strong basic reaction, and exhibits also the other characteristics of hydroxidion. This is due to the fact that the ion CO_3'', which is the immediate product of dissociation of the salt, reacts with the water of the solution in accordance with the equation $CO_3'' + H_2O = HCO_3' + OH'$. Reactions of this kind have been discussed at length in connection with phosphoric acid (p. 363).

Potassium carbonate is a convenient starting substance for the preparation of other potassium salts. On the one hand, most free acids form the corresponding salts with potassium carbonate, with evolution of carbon dioxide. Carbonic acid is, as has already been shown (p. 388), a very weak acid, and this reaction therefore takes place with great readiness and completeness. On the other hand, carbonic acid forms very difficultly soluble salts with almost all metals except those of the alkali group. If, therefore, salts of those metals with any acids are brought together with potassium carbonate, the solubility product of the corresponding metallic carbonate is exceeded, and the latter is precipitated, while the potassium salt of the acid remains in solution, from which it can be obtained by evaporation after filtering off the precipitate.

Potassium Bicarbonate.—In the aqueous solutions of potassium carbonate, the ion CO_3'' is, as has already been mentioned, partly converted by the action of the water into the ion HCO_3'; the quantity transformed, however, amounts to only a few per cent of the total quantity. If, however, carbon dioxide be passed into the solution, the reaction $CO_3'' + CO_2 + H_2O = 2HCO_3'$ takes place almost completely, and a solution of the acid or primary potassium carbonate, $KHCO_3$, is formed. If the solution was concentrated, the solubility product of this salt is exceeded, and it is deposited in monoclinic crystals.

The solution reacts fairly neutral, but still not so definitely as that of a salt of a strong acid, and dilute solutions exhibit even a distinctly alkaline reaction. This is due to the fact that the first ion of the dibasic carbonic acid, although much stronger than the second, is, nevertheless, the ion of a very weak acid. Hydrolysis therefore occurs, hydrion from the solvent water uniting with HCO_3' to form undissociated carbonic acid H_2CO_3, or its anhydride CO_2. The presence of the last compound can be easily demonstrated by heating the solution; even before the boiling point has been reached, bubbles of carbon dioxide are evolved. In proportion as carbon dioxide escapes, more is formed. By reason, however, of the increasing concentration of hydroxidion, the equilibrium changes so as to become more and more unfavourable to carbon dioxide, and the evolution of the gas finally sinks practically to zero. The ratio of the concentrations at which this occurs depends on the degree of dilution, more carbon dioxide being evolved the greater the dilution.

Although, therefore, acid potassium carbonate is partially decomposed in aqueous solution, the pure salt is obtained by the careful evaporation of such a solution. This is due to the fact that when some of the pure salt has separated from the saturated solution, the decomposition of the solution must become reversed, for by the separation some of the undecomposed salt is removed from participation in the equilibrium, and equilibrium can be re-established only by more of the salt being formed. This goes on until the solution is evaporated to dryness, provided there is no deficiency of one of the components, especially carbon dioxide. In order, therefore, that pure salt may be obtained with certainty, an excess of carbon dioxide must be maintained in the solution, by passing some of this gas into the solution from time to time.

The above relations receive an application in numerous similar cases.

On heating dry potassium bicarbonate, also, decomposition occurs, and, in this case, proceeds further, there remaining ultimately a residue of pure normal carbonate. The process is represented by the equation $2KHCO_3 = K_2CO_3 + H_2O + CO_2$. It proceeds in a perfectly similar manner to the evaporation of a volatile liquid, and at each temperature a quite definite pressure is established; on this pressure the amounts of the two solid substances present, normal and acid potassium carbonate, have no influence. If for any given temperature that pressure has been established at which equilibrium exists, and if it be now attempted to diminish the pressure by increasing the volume, more of the acid carbonate decomposes until the pressure has again reached the former value. If, on the other hand, the volume is diminished, the pressure is only temporarily increased; carbon dioxide and aqueous vapour are absorbed until the original pressure is again established.

* Such a behaviour follows from an application of the phase law. We are here dealing with three components, and there are three phases present, viz., the two solid salts and the gaseous mixture. Consequently, there still remain two degrees of freedom, and at each temperature we can obtain different pressures by suitably changing the composition of the gas mixture. So long, however, as this mixture is evolved from the bicarbonate itself, its composition is constant, since it consists of equal molecular amounts, and therefore, also, equal volumes of carbon dioxide and aqueous vapour. We have thereby disposed of one of the degrees of freedom, and only one now remains, so that to each temperature there belongs a definite pressure.

* If, on the other hand, the composition of the vapour is changed, the pressure can also be changed even at a constant temperature. The law for this follows from an application of the theory of chemical equilibrium. If in the equation $2KHCO_3 = K_2CO_3 + H_2O + CO_2$ the concentrations of the four substances are designated respectively by a, b, c, and d, we have the equation $a^2 = k . bcd$, where k is the equilibrium constant (p. 327). Of these magnitudes, a and b are constant, since they refer to solid substances; collecting all the constants, there follows $c . d = K$, where K is the new constant, which is still dependent

on the temperature but is no longer dependent on the concentrations or amounts of the participating substances. Hence it follows that if, at a given temperature, the concentration of the aqueous vapour in the gas mixture is increased, that of the carbon dioxide must decrease, and *vice versa*, until the product of the two concentrations again assumes its former value. The bicarbonate, therefore, will undergo less decomposition in an atmosphere of aqueous vapour or of carbon dioxide than in a vacuum or in a foreign gas. This rule is a general one for decompositions of this kind.

Potassium Sulphate, K_2SO_4, crystallises in anhydrous, rhombic pyramids which, owing to the presence of hemihedral faces, look as if they belonged to the hexagonal system. Such imitations, which are comparable with the mimicry of the lower animals, are not rare in the case of crystalline substances; their significance has not yet been pointed out.

The salt is rather difficultly soluble in water, and the solubility increases almost linearly with rising temperature.

Potassium sulphate occurs as a constituent of the double salts in the German potash beds, and is obtained in the pure state by a crystallisation process. It is used in the preparation of alum (cf. aluminium) and of potassium carbonate, and as a manure.

When warmed with sulphuric acid it is converted into the acid potassium sulphate, in accordance with the equation $K_2SO_4 + H_2SO_4 = 2KHSO_4$. The latter is a salt which is readily soluble in water, and melts at 200°. On being further heated it loses water and passes into potassium pyrosulphate $K_2S_2O_7$ (p. 291), which decomposes at a red heat into normal salt and sulphur trioxide. This is a method of preparing the anhydride from sulphuric acid; since the direct preparation of the latter (p. 283) was introduced this process has lost its technical importance.

Acid potassium sulphate is used in analysis because at the temperature of fusion it has a powerful solvent and decomposing action on many substances, especially basic oxides and silicates. Its action is considerably superior to that of sulphuric acid. This is due to the fact that the temperature can be raised to a higher degree; for in the case of sulphuric acid a limit is set by the boiling point, 340°.

The aqueous solution of potassium bisulphate has a strong acid reaction, because the anion of this salt, HSO_4', partially dissociates into $H^{\cdot}$ and SO_4''; hydrion is thereby produced in the liquid, and exhibits its reactions. Accordingly, the ions of the normal sulphate, $2K^{\cdot}$ and SO_4'', are also present in the solution, and since this salt is less soluble it may be deposited under favourable conditions. This is the case, for example, when a not quite saturated solution of the acid salt is prepared at the boiling temperature, and the liquid allowed to cool. The same reaction occurs when the acid salt is allowed to lie in the air on a porous surface, *e.g.* on a brick. The solution, rich in sulphuric acid, is drawn into the brick, and the normal potassium sulphate remains behind.

Potassium Persulphate, $K_2S_2O_8$. The formation of this salt in the electrolysis of acid potassium sulphate has already been described (p. 293). It is rather difficultly soluble in water, and exhibits the oxidising actions of persulphuric acid; it therefore finds application in photography and in some other departments of the arts. When pure, it can be preserved; but its decomposition appears to be catalytically accelerated by certain substances, so that impure specimens rapidly become moist in the air and deliquesce, oxygen being evolved and acid sulphate being formed: $2K_2S_2O_8 + 2H_2O = 4KHSO_4 + O_2$.

Potassium Sulphite.—Of the different salts which sulphurous acid can form with potassion, potassium pyrosulphite, $K_2S_2O_5$, is the only one of importance. It is obtained by saturating a warm, concentrated solution of potassium carbonate with sulphur dioxide; on cooling, the salt crystallises in large, transparent, and anhydrous crystals. It is employed in photography, and has the advantage that it oxidises only very slowly in the air, while other sulphites are much less stable in this respect. It dissolves in water, and yields a solution of acid sulphite, *i.e.* a solution containing the ions HSO_3' and $K^{\cdot}$.

Potassium Sulphide.—If a solution of caustic potash is saturated with sulphuretted hydrogen, so much of this is absorbed that the salt KHS, potassium hydrosulphide or the acid salt of sulphuretted hydrogen, is formed. By evaporation it can be obtained as a very deliquescent salt, containing $\frac{1}{2}H_2O$ of crystallisation. If as much caustic potash is added as had been originally taken, and the solution evaporated, potassium sulphide, K_2S, which is also very soluble, can be obtained with $5H_2O$ of crystallisation. Anhydrous potassium sulphide is obtained by the reduction of potassium sulphate with pure charcoal: $K_2SO_4 + 4C = K_2S + 4CO$. It is, however, very difficult to obtain a pure product, because the fused potassium sulphide attacks vessels of all kinds and becomes contaminated with the constituents of these.

The aqueous solution of potassium sulphide has a strongly alkaline reaction, and for the most part does not contain the ions $K^{\cdot}$ and S''. On the contrary, the latter react with the solvent water and form HS' and OH', so that the solution contains hydroxidion in large quantity. Here, as in all such cases, we are dealing with a chemical equilibrium in which all possible ions are present—sulphidion, S'', therefore, as well; the amount of the latter is, however, very small.

The solutions of potassium sulphide rapidly oxidise in the air, the sulphide being converted into the potassium salts of the oxygen acids of sulphur. In the first instance, thiosulphanion is formed from the ion HS' by the absorption of oxygen: $2HS' + 2O_2 = S_2O_3'' + H_2O$.

In analytical chemistry, potassium sulphide is employed in order to obtain those difficultly soluble metallic sulphides which are decomposed by acids: *e.g.* $K_2S + FeCl_2 = FeS + 2KCl$. For this purpose, it is of no consequence that only a small amount of sulphidion is present in the solution, for when this is removed in the precipitate, a fresh quantity is immediately formed from HS′ and OH′. For the above reaction, however, potassium sulphide is less used than the similarly acting ammonium sulphide, since the latter, or its products of transformation, can be much more readily removed from the analysis than can potassium sulphide.

If a solution of potassium sulphide is warmed with sulphur, large quantities of the latter are taken up, and the potassium salts of the ions S_3'', S_4'', and S_5'' are formed, according to the amount of sulphur dissolved. They are all characterised by the fact that they give yellow-red solutions. If the liquids be poured into hydrochloric acid, the corresponding acids H_2S_2 to H_2S_5 separate out as oily liquids, which very readily decompose into sulphur and sulphuretted hydrogen, and are not known in the pure state. If, on the other hand, the hydrochloric acid is added to the sulphide solutions, sulphur and sulphuretted hydrogen are immediately obtained. The former is very finely divided, and constitutes milk of sulphur (p. 256).

* The peculiar difference of these two reactions is due to the fact that, in the first case, the acids formed, H_2S_2 to H_2S_5, are always in contact with the acid liquid; in the second case, with the liquid containing potassium sulphide. The latter, however, acts catalytically on the polysulphides of hydrogen, and accelerates their decomposition into sulphuretted hydrogen and sulphur.

Potassium Nitrate, KNO_3, or saltpetre, is, along with common salt, one of the longest known salts. The reason of this is that the materials necessary for its formation (*vide* p. 318), viz. nitrogenous animal matter (dung) and potash salts (ashes), accumulated around the dwellings of man even at a period of very low civilisation, so that the salt produced soon presented itself to observation. The nitranion is formed from ammonia under the action of certain bacteria (saltpetre bacteria), which promote the oxidation of the ammonia by the oxygen of the air. If no compounds of potassium are present, other nitrates are formed, especially calcium nitrate, by means of the almost never-failing calcium compounds.

From such places of its formation, whether formed by chance or purposely, the saltpetre is obtained by extraction with water, whereby use is again made of the principle of counter-currents (p. 455). It is separated by crystallisation from the other substances which are extracted along with it, an operation which is greatly facilitated by the great difference of its solubility at different temperatures.

In the pure state, potassium nitrate is a colourless salt, which crystallises in rhombic, anhydrous crystals. The crystals often mechanically enclose portions of the "mother liquor," *i.e.* the solution from which they are formed, cavities being left in the crystals in their growth, in which the solution is then enclosed. The enclosed liquid cannot be got rid of by drying the crystals. These liquid enclosures contain all the impurities of the mother liquor, so that the salt obtained is less pure than the substance of the crystals itself; their formation must therefore be, as far as possible, avoided. From this there follows the rule that for purposes of purification, not large but small crystals must be formed; this happens when the crystallising liquid is quickly cooled and kept in movement, so that the crystals formed are separated from one another, and by the breaking off of small particles give rise to new crystals.

At the present time, saltpetre is chiefly obtained from sodium nitrate or Chili saltpetre, solutions of this salt being mixed with solutions of potassium chloride. From the mixed solution which contains the ions $K^{\cdot}$, $Na^{\cdot}$, Cl', and NO_3', that salt will be first deposited whose solubility product is first exceeded. On comparing the solubility curves of the four salts which are represented in Fig. 105, the solubilities being given in moles, it is seen that at higher temperatures sodium chloride has the lowest molecular solubility; on evaporating down the solution by heat, common salt will, therefore, be deposited. When the concentration of the ions $Na^{\cdot}$ and Cl' has thereby become so small that their product approaches the value of the solubility product, the solution is allowed to cool down. At low temperatures potassium nitrate is obtained. The mother liquor, from which a large part of the ions $K^{\cdot}$ and NO_3' have now disappeared, can be again made to deposit sodium chloride at the temperature of boiling, and in this way it is possible to effect the complete transformation of the two salts.

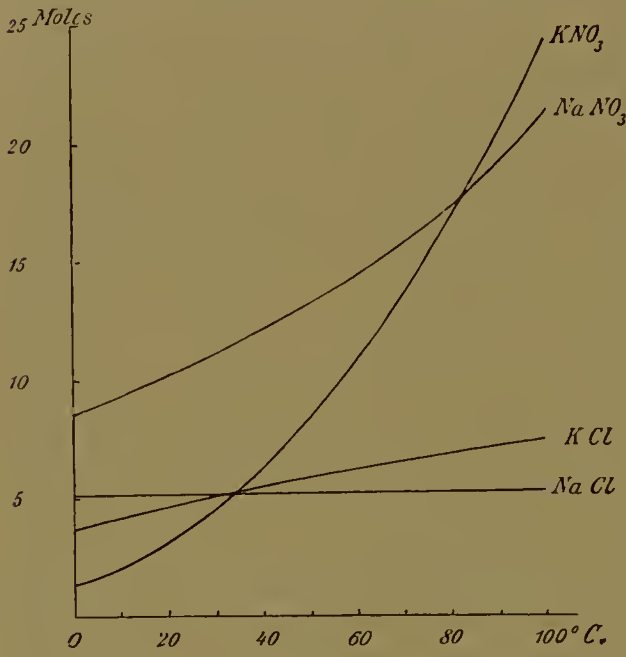

Fig. 105.

The same method of purification is used for the crude saltpetre obtained by the action of bacteria, since in this case also the chief impurity is generally common salt.

On account of the large amount of oxygen it contains, and which it readily yields up, saltpetre is used for the preparation of mixtures which burn without the aid of the atmospheric oxygen. Such mixtures are used in the manufacture of fireworks, and as explosives for blasting and shooting. Whereas, formerly, saltpetre was almost the only substance which could be used for such purposes, a large number of other substances which can be employed are now known, so that the importance of potassium nitrate has greatly decreased compared with formerly, especially as it has been replaced by the cheaper sodium nitrate in the preparation of nitric acid and its derivatives.

The most important explosive mixture was for long that consisting of saltpetre, sulphur, and charcoal, and called *gun-powder*. Such a mixture burns suddenly when ignited, the sulphur and the carbon combining with the oxygen of the saltpetre; gaseous carbon monoxide and nitrogen are thereby formed, and the sudden increase of volume or of pressure thus produced, is the cause of its action in blasting and shooting. It is a case of the conversion of chemical energy into mechanical, and the importance of gunpowder and all such substances depends on the fact that considerable amounts of transformable chemical energy can be obtained in a very short time from comparatively small amounts of such substances.

The three constituents of gunpowder are mixed in such a way that the reaction $2KNO_3 + S + 2C = K_2SO_4 + N_2 + 2CO$ chiefly occurs. According to the combining weights of the substances named, the proportions would be 202 : 32 : 24, or 1 : 0·159 : 0·119 ; the proportions which are actually used vary, but are, on the average, 1 : 0·16 : 0·16. In the preparation, however, pure charcoal is not employed, but a product obtained by the very slight carbonisation of thin pieces of wood, which still contains large quantities of hydrogen and ash. For this reason, the chemical process pursues a more or less different course from that given in the equation; in particular there are formed, besides potassium sulphate, compounds containing less oxygen and even potassium sulphide.

The three moles of gas formed in accordance with the simple equation occupy, under atmospheric pressure and at 0°, a volume $3 \times 42{,}400$ cc., while the 258 gm. of the mixture occupy scarcely 100 cc., *i.e.* about $\frac{1}{700}$th of the former volume. The very considerable pressure which thereby results, and which is produced by the combustion of the gunpowder in a confined space, is further largely increased by the fact that owing to the heat of reaction, the temperature rises to considerably above a red-heat. From the heats of formation of the reacting substances, the heat of reaction can be calculated to be 686 *kj*. If this amount of energy were completely convertible into kinetic energy, 1 gm. of gunpowder would suffice to project a ball 1 kilogm. in weight with a velocity of 16×10^4 cm./sec., or 1·6 kilometre/sec. As a matter of fact, only a portion of the energy is utilised, since the gases produced leave the gun at a fairly high temperature; besides, it is not yet known what part of the total energy is present as free energy, *i.e.* is convertible into other forms of energy (p. 208).

Saltpetre melts at 339°, and at a higher temperature it loses oxygen, and passes into potassium nitrite (which see). This reaction is of historical interest, because Scheele, the discoverer of oxygen, first obtained the pure gas in this manner.

* In order to show this evolution of oxygen, saltpetre is melted in a thin-walled tube over a strong flame, and the liquid is heated until the evolution of gas is observed. If, now, small pieces of sulphur are thrown on the fused mass, they burn with an exceedingly dazzling light, and potassium sulphate is formed, as well as lower oxidation compounds of nitrogen, which escape in the form of brown fumes.

Potassium Nitrite, KNO_2, was for a long time the most largely used salt of nitrous acid, and was employed for all purposes for which that acid was used, more especially in the preparation of artificial dyes. In recent times it has been replaced by the cheaper sodium nitrite. Potassium nitrite is a yellowish salt, very readily soluble in water, which is obtained from potassium nitrate by heating this with reducing substances, usually with lead (p. 329). Since it does not crystallise well, it is generally sent into the market cast into sticks. The aqueous solution reacts alkaline, for nitrous acid is a weak acid, and its salts are appreciably hydrolysed in aqueous solution.

Potassium Silicate.—Caustic potash and potassium carbonate fuse together in all proportions with silicon dioxide to form glassy masses which, if they do not contain too much of the latter substance, dissolve in large amounts on prolonged boiling with water, forming syrupy liquids. It is not possible to detect any definite compounds in these. From the alkaline reaction of the solutions, it can be inferred that the potassium silicate present is partially dissociated hydrolytically; by means of dialysis it is found that a portion of the silicic acid is present in the colloidal state, and the electrical conductivity shows that a given solution, on being kept, undergoes change in such a way that more hydroxidion and colloidal silicic acid continue to be formed, for the conductivity increases[1] when the solution is kept and external influences carefully excluded.

The concentrated solution of potassium silicate is placed on the market under the name of *water glass*, since in the air it dries up to a glassy mass. It effects a kind of silicification in substances soaked in or painted over with it, and is therefore extensively applied in the arts.

Potassium Silicofluoride.—As has already been mentioned, solutions of hydrofluosilicic acid give, with potassion, precipitates of the very difficultly soluble salt K_2SiF_6. The reaction must be carried out in acid solution, since alkaline liquids decompose hydrofluosilicic acid (p. 427).

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[1] Hydroxidion causes at least twice as great a conductivity as any other anion in equivalent amount, as has been found from the investigations of this point. Since the formation of other anions of great conductivity is excluded here, it must be concluded from the increase of the conductivity that there is an increase of hydroxidion in the manner given.

The precipitate of the potassium salt has an unusual appearance, for it is almost invisible in the liquid, and when it is observed in some quantity in a transparent vessel, it forms a translucent mass exhibiting a play of pale colours which reminds one of opal. The cause of this is that the index of refraction of this salt is very nearly the same as that of water. If there is placed in a liquid a solid powder which has nearly the same power of refraction as the liquid, interference colours are produced by the partial mutual extinction of the different rays, and the light which remains is correspondingly coloured. The variation in the size of the particles is the reason that different rays are extinguished, and to this the iridescence is due.

Very similar to this salt is the potassium salt of hydrofluoboric acid, KBF_4 (p. 431).

Potassium Cyanide.—On heating potassium with substances which contain nitrogen along with carbon, potassium cyanide, KCN, the most important salt of cyanidion, is formed. It was formerly chiefly prepared by heating potassium carbonate with nitrogenous charcoal, obtained by the carbonisation of horn, leather, or other animal substances. Since potassium carbonate and charcoal yield metallic potassium, the reaction is the same as the former mentioned. The product contains very impure potassium cyanide, and since this does not readily crystallise and is therefore difficult to purify, the potassium cyanide present was converted by heating the aqueous solution with iron compounds into a salt of complicated composition, potassium ferrocyanide, or yellow prussiate of potash (*vide* iron), which can be easily purified by crystallisation. From this, pure potassium cyanide is again recovered.

At the present time, when a large demand for potassium cyanide has arisen for the purposes of gold extraction, other methods of preparation have been sought for. Cyanogen compounds are formed, in general, at very high temperatures when the elements carbon and nitrogen are present (p. 413); thus, for example, considerable quantities of potassium cyanide are formed in the iron blast-furnaces. On the manufacturing scale, it can be obtained by passing ammonia over a mixture of potassium carbonate and charcoal at a high temperature. Further, barium cyanide is formed from a mixture of barium carbonate, charcoal, and free nitrogen at the temperature of the electric furnace; the product is converted into potassium cyanide by means of potassium carbonate or sulphate.

Potassium cyanide is a white, very soluble salt, whose aqueous solution has an alkaline reaction and smells strongly of hydrogen cyanide. This is due to the fact that hydrocyanic acid is an extremely weak acid, whose salts are partially dissociated hydrolytically in aqueous solution; the carbonic acid of the air also has a decomposing action on the salt. Potassium cyanide is a powerful poison; in spite of this it is largely employed in the arts. It is used in photography to dissolve silver salts, also in electroplating with metals, especially in gilding and silvering, and finally, in very large amounts, for extracting the finely divided gold from the auriferous beds, especially in South Africa. Since all these applications depend on the formation of definite compounds with the heavy metals named, they can be explained in detail only under these metals.

In analytical and preparative chemistry, potassium cyanide is used as a powerful reducing agent, which allows of many metals being separated from their oxides and sulphides at its temperature of fusion. It is converted in the process into potassium cyanate and potassium thiocyanate respectively.

As to *potassium cyanate*, the essential points have already been given (p. 415). It is a white salt readily soluble in water, which on being acidified evolves carbon dioxide, while an ammonium salt is formed in the solution. This reaction, which depends on the transformation of cyanic acid, has also been already explained at the place cited.

Potassium thiocyanate, or sulphocyanide, KSCN, is the salt chiefly used in the applications of thiocyananion, SCN'. It is a colourless salt which readily dissolves in water, at the same time producing a very considerable fall of temperature. It is easily obtained by heating potassium cyanide with sulphur.

Potassium Oxalate.—Oxalic acid forms with potassium not only the two salts which, according to the dibasic nature of the acid, are to be expected, but also another salt which can be regarded as a compound of oxalic acid with acid potassium oxalate. Of the salts of oxalic acid, those with potassium are the best known, because they occur in the juices of various plants, from which they were early prepared, and have led to the knowledge of oxalic acid.

Normal potassium oxalate, $K_2C_2O_4 + H_2O$, is a white salt soluble in water, and is used in photography.

Acid potassium oxalate, $KHC_2O_4 + \frac{1}{2}H_2O$, is called salt of sorrel because it was first obtained by evaporation and crystallisation from the juice of the wood-sorrel. It is less soluble than the normal salt and is used for removing iron and ink stains, since it converts iron salts into soluble (complex) compounds.

Potassium tetroxalate is the name given to the salt $KHC_2O_4 \cdot H_2C_2O_4 + 2H_2O$, which is easily obtained by mixing one of the previous salts with the necessary excess (or rather more) of oxalic acid in warm concentrated solution. It then quickly crystallises out, since it is rather difficultly soluble. This salt is used in volumetric analysis in place of free oxalic acid, because it does not effloresce so readily as the latter, and allows therefore of definite amounts being accurately weighed out.

* If two equal amounts of acid potassium oxalate are weighed out and one converted, by heating, into potassium carbonate and then dissolved along with the second portion, a liquid having a perfectly neutral reaction is obtained, after the carbonic acid is boiled off. This

is a proof that in the acid oxalate exactly half as much potassium is contained as is necessary for the preparation of the normal salt. In this simple manner, the law of multiple proportions (p. 140) was proved by Wollaston as early as the year 1808.

Other Compounds of Potassium.—On account of its great tendency to form ions, potassium can form non-saline compounds only in the absence of water, and all these compounds possess the property of decomposing in contact with water in such a way that potassion is formed along with the corresponding other substances. Of such compounds the following have to be mentioned.

Potassium peroxide is formed by the combustion of potassium in dry oxygen. Its composition varies between the amounts represented by the formulæ K_2O_3 and K_2O_4. In water it dissolves with evolution of oxygen and formation of hydrogen peroxide.

Potassium hydride, K_2H or K_4H_2, is formed when hydrogen is passed over potassium at a temperature of about 300°. It forms a mass with a metallic lustre, and again loses its hydrogen at fairly high temperatures. The pressure of the hydrogen increases with rise of temperature, but is not independent of the degree of decomposition, as in the case, for example, of salts with water of crystallisation, but diminishes as the decomposition proceeds. This is due to the fact that at these temperatures the substance is *liquid*, and is a mixture of potassium and potassium hydride of varying composition. Just as the vapour pressure, for example, of hydrated sulphuric acid varies with the proportions of water and sulphuric acid in the liquid, and diminishes, therefore, when, at a given temperature, an increasingly large part of the water is allowed to pass into vapour, so the pressure of the hydrogen from the liquid mixture diminishes in proportion as the latter becomes less rich in hydrogen.

This follows on applying the phase law to the case in question. There are two components and two phases, viz. the liquid mixture and the hydrogen gas. Consequently there are still two degrees of freedom present, *i.e.* at a given temperature, different pressures can exist depending on the composition of the liquid.

With water, potassium hydride forms potassium hydroxide and hydrogen. It very readily ignites in the air.

By the action of metallic potassium on ammonia gas, a greyish green mass of *potassamide* is formed in accordance with the equation $2K + 2NH_3 = 2KH_2N + H_2$. This compound can be regarded as ammonia, in which one combining weight of hydrogen is replaced by potassium. It is very reactive, and is used for the preparation of other nitrogen compounds, especially in organic chemistry. By the action of nitrous oxide it is converted into the potassium salt of hydrazoic acid: $KH_2N + N_2O = KN_3 + H_2O$ (p. 346). With water, potassamide decomposes, forming potassium hydroxide and ammonia: $KH_2N + H_2O = KOH + NH_3$.

CHAPTER XXI

SODIUM

General.—The chemical relations of sodium are very similar to those of potassium, so that for chemical purposes the one metal can in most cases replace the other. This holds good especially for those reactions in which the ions come into account. The reason of this is that sodion also represents by far the most stable state as compared with metallic sodium, and the reactions of this element, as in the case of potassium, are therefore chiefly characterised by the fact that the ion is formed with especial readiness from the metal, but the metal only with difficulty from the ion. Since, further, the state of the salts in the solid form approaches more nearly to that of the ions than to that of the metal, sodium, like potassium, will be easily transformed from one of its salts into another, but will be converted only with difficulty from a salt into the metal or a compound closely related to this.

Metallic sodium does not occur in nature, since it would everywhere have an opportunity of exercising its tendency to pass into sodion. Sodion, however, has an extensive distribution, and, along with chloridion, with which it occurs in sea-water, it may be regarded as the most abundant ion in those parts of the earth's surface which are accessible to us.

In more remote times, the compounds of the two elements potassium and sodium were confused with one another. When it was learned how to distinguish them (p. 436), caustic potash was known as the vegetable, and caustic soda as the mineral alkali, because the former was obtained chiefly from the ash of plants, the latter from common salt. It was later found by Klaproth that both elements are present in the mineral kingdom. So far as the vegetable kingdom is concerned, an essential difference does certainly exist between the two elements; for compounds of potassium must be present in considerable amount in plants in order that these may develop normally. Sodium compounds, it is true, are never wanting in plants, but they are more chance constituents which pass into the plants from the soil, in which they are always present, and seem not to play any particular part in them.

Although therefore, normal vegetation may be hindered by an *entire* exclusion of sodium compounds (although no indubitable evidence on this point exists), it is certain that the quantities of sodium which may possibly be necessary for a plant are incomparably smaller than the amounts of potassium which are indispensable.

The cause of this difference may be found in the following circumstance. Whereas the soil in which plants thrive has the remarkable property of withdrawing dissolved potassium compounds from solution, and retaining them in such a way that they can be taken up only in a very slight degree by water, the behaviour is quite different with respect to the sodium compounds. These are not taken up and retained by the soil, but filter through without difficulty. Whereas, therefore, the amount of potassium compounds in the soil is considerable and almost independent of chance conditions, the amount of the sodium compounds is subject to variation and to chance. On the principle of the survival of the fittest, it is intelligible that the chemical requirements of the plants, the satisfaction of which is effected by an alkali metal (or its ion), should be supplied by the constantly present potassium, since organisms whose life depended on utilising sodium compounds would die out by reason of the readily occurring lack of these.

The accumulation of sodion in sea-water is due to the same cause. When in the decomposition of the rocks by water and carbonic acid, described on p. 421, the alkali metals pass into solution in the form of their ions, they follow, in the first instance, the general movement of the water towards the ocean. The potassium, however, is mostly retained on the way, because it is seized hold of by the soil; the sodion, however, passes on unhindered to the sea, and is deposited again in the solid form only in rare cases, viz., when the sea-water is concentrated by evaporation until the solid salt forms.

Cases of this have occurred, especially in former geological periods, nd have given rise to beds of rock-salt or sodium chloride, the two ons which are present in greatest abundance in sea-water having been leposited together as solid salt.

Metallic Sodium.—We have already, on several occasions, become icquainted with metallic sodium as a silver white, soft, and readily usible metal, which reacts energetically in contact with water, and just s readily forms compounds with many other substances. It behaves, n general, quite similarly to potassium, from which it is distinguished y the somewhat inferior violence of its reactions.

Thus, sodium does not take fire when thrown on water; it does so, owever, if its motion and the cooling which is thereby effected is preented. This happens when the metal is placed on wet paper or on an queous jelly of glue or of starch. The evolved hydrogen as well as a ortion of the metal then burns with a bright yellow flame, and all the lames in a room in which such a combustion has occurred burn distinctly yellow for a considerable time. This is due to the fact that the dissipated sodium compounds colour the flames yellow, even when present in the minutest quantities (p. 84).

Sodium melts at 97·5°, and boils at about 740°. The accurate determination of its vapour density is difficult, but the experiments which have been made agree in showing that the molar weight of sodium vapour is 23, or equal to the combining weight. This identity is a general property of the metals, so far as these are known in the vapour form, and less doubtful cases of the confirmation of this rule will be given later (cf. zinc).

By mixture with other metals, the melting point of sodium is lowered. This is especially well seen on adding potassium; in this way alloys can easily be obtained which are liquid at the room temperature.

* This phenomenon is by no means to be explained as a consequence of chemical combination between the metals; on the contrary, it is the simple consequence of the perfectly general fact that the melting point of every substance is lowered by the addition of such substances as are soluble in the liquid form of the first substance. If the melting point of the pure substance is not too high above room temperature, the lowering can occur to below this temperature, and the phenomenon in question makes its appearance.

The first preparation of metallic sodium was effected by Davy by means of the voltaic pile at the same time as that of potassium (p. 436). Shortly afterwards the method of obtaining it by distillation of sodium carbonate with charcoal was discovered, corresponding to the method mentioned under potassium. Since about 1860, sodium has been obtained on the large scale by this method, the metal being used for preparing aluminium. Recently, however, the electrical method has again been adopted, and sodium is obtained by the decomposition of sodium hydroxide by means of the electric current. By reason of the comparatively small cost of electrical energy, combined with the good yield obtained, sodium can be obtained more cheaply by this than by the old method. It is remarkable that this method is identical with that by which sodium was first prepared, for on that occasion also, sodium hydroxide was the original substance.

* The electrolysis is carried out in iron pots divided by permeable partitions. At the anode oxygen escapes, at the cathode sodium and hydrogen are formed. The separated metal is lighter than the liquid hydroxide, and therefore floats to the surface; it is skimmed off from time to time.

* Sodium can also be obtained by the electrolysis of fused sodium chloride. Much difficulty, however, is caused by the high melting point of this salt. The melting point can be lowered by mixing it with potassium chloride; mixtures of sodium with a little potassium are then obtained, but not the pure metal.

Metallic sodium is largely used in the arts and in the laboratory. Its former importance for obtaining other, difficultly reducible metals, has been lost, since the object can generally be attained more readily by means of magnesium or aluminium, or by the electrolytic method. It is used, however, as a powerful reducing agent in many reactions in organic chemistry, and for obtaining reactive intermediate products.

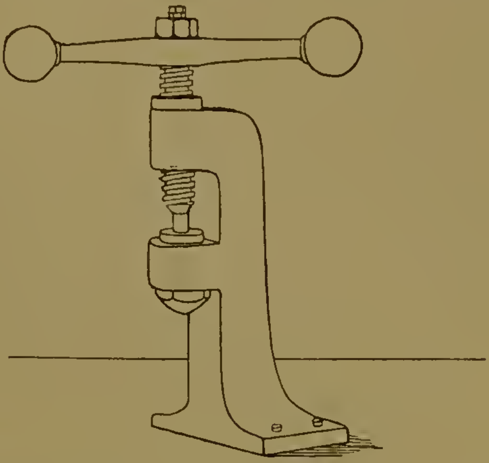
FIG. 106.

For these purposes, the metal is best employed in a condition in which it offers a large surface. Since, on account of the softness of the metal, it cannot be reduced to small pieces by blows or by filing, it is forced, by means of an iron screw press (Fig. 106), through narrow openings, and is thus obtained in the form of wire or of ribbon, according to the shape of the opening. Since in this state the metal very rapidly oxidises in the air, the wire is allowed to fall directly into the liquid on which it is to act, or it is collected in a liquid which does not contain oxygen. Petroleum, which is usually employed for this purpose, has the disadvantage that it is difficult to remove; for chemical purposes, therefore, it is better to use readily volatile hydrocarbons obtained from the low-boiling portions of petroleum (so-called petroleum benzine or petroleum ether).

Sodion.—The description of the general characteristics which was given for potassion, can be applied almost word for word to sodion. This also is a monovalent ion, which is colourless, and forms, almost exclusively, readily soluble salts. In this respect it is even superior to potassium, since there is scarcely a difficultly soluble salt of sodium known by means of which this ion could be readily and certainly detected. Further, there is no compound of sodium known which is formed in aqueous solution, by the colour of which it is possible to detect sodion. This is due to the fact that in all aqueous solutions which contain sodium, that element is present in the form of sodion, or, in other words, no sodium compound can be dissolved in water without being converted for the most part into sodion.

The detection of sodium in analysis would, therefore, be a matter of difficulty if it were not that there is another property by means of which it is rendered very easy. This is the yellow coloration which is imparted to a flame through the presence of sodium (p. 84). To what form or compound of sodium this yellow light has to be ascribed, has not yet been determined with certainty; for the purposes of analysis the fact is sufficient that all sodium compounds give rise to this phenomenon in flames containing oxygen.

To carry out the experiment, the substance to be investigated is introduced into the non-luminous flame of the Bunsen burner; if it is in the form of a liquid solution, this is evaporated, and the residue tested. As a carrier for the substance, a thin platinum wire is used, the end of which is bent into the form of a loop.

It is soon found that the faint blue colour of the Bunsen flame is coloured yellow by almost all substances. If the platinum wire has lain for some time in the air so that it is covered with some dust, it also imparts a yellow coloration to the flame, but this coloration soon disappears. It is only necessary, however, to draw the wire, cleaned by heating in a flame, between the fingers, when it again acquires the above property for some moments.

This is a consequence, on the one hand, of the wide distribution of sodium, and, on the other hand, of the great sensitiveness of the flame coloration. By evaporating some sodium into a large space and determining the point at which a Bunsen flame burning in this space just began to show the coloration, the fact could be established that less than 3×10^{-10} gm. of sodium are sufficient to give this reaction.

The difficulty which is caused by the wide distribution of small quantities of sodium in cases where we are dealing with the detection of comparatively large amounts of this element in a specimen given, can be overcome by observing the *length of time* during which the yellow coloration lasts. Whereas the accidental traces of sodium in dust and in almost all substances give rise to only a feeble coloration which quickly disappears on account of the volatility of the sodium compounds, appreciable quantities of sodium, of the order of 1 milligm., produce a brightly luminous yellow flame which lasts for a considerable period with undiminished brightness. By a few experiments made with known quantities of sodium compounds, the chemist learns once for all to distinguish between these phenomena.

This method, of course, cannot be employed for the quantitative determination of sodium. In this case the two alkali metals, potassium and sodium, are generally separated as salts of the same nature (*e.g.* as chlorides), weighed together, and the amount of potassium determined by means of the methods described on p. 444; the difference gives the amount of sodium.

* If it is known that only these two elements are present, the method of *indirect analysis* may be employed. This is based on the fact that different amounts of the corresponding compounds of the two elements are required in order to react with equal quantities of another substance. Accordingly, also, they yield different amounts of corresponding compounds when they are transformed together. A few examples will make this clear.

Since the combining weight of sodium hydroxide or caustic soda is 40·06, and that of caustic potash 56·15, 1 gm. of the former will require 1/40·06 lit. or 24·97 cc., and 1 gm. of the latter will require 1/56·15 lit. or 17·80 cc., of normal acid solution for complete neutralisation (p. 187). A mixture of the two hydroxides will require an amount intermediate between these two. In 1 gm. of the mixture, let there be x gm. of caustic soda, and therefore $(1-x)$ gm. of caustic potash, then the quantity of acid used will be $24·97x + 17·80\,(1-x)$ cc. If, therefore, the quantity of acid, S, necessary for neutralisation of the mixture is determined, the magnitude x may, conversely, be calculated. For from the equation $24·97x + 17·80\ (1-x) = S$, there follows $x = (S - 17·80)/7·17$.

If, for example, 21·40 cc. acid have been used, there follows $x = 0·502$.

* Similar relations hold in the combined transformation into other compounds. For example, let a mixture of the two chlorides be given, and let these be converted into the corresponding sulphates by evaporation with sulphuric acid and strongly heating. The ratio of the weights $2NaCl : Na_2SO_4$ would then be equal to 117·02 : 142·18, or 1 : 1·215, while in the case of potassium the ratio would be 149·18 : 174·34 or 1 : 1·169. If from 1 gm. of an unknown mixture of the two chlorides the weight S of the mixed sulphates is obtained, there holds the equation $1·215x + 1·169(1-x) = S$, and $x = (S - 1·169)/0·046$.

* If we denote, generally, a number of this kind which corresponds to the reaction of the sodium salt by n, and by k the corresponding number for the potassium salt, while S is the number for the mixture, we obtain the general equation $x = (S-k)/(n-k)$.

* Such an indirect analysis is always less certain than a direct one. This is due, on the one hand, to the fact that the supposition must be made that the given mixture contains only the two substances supposed, and no others; and, on the other hand, to the fact that the accuracy of the value sought, x, is, necessarily, less than that of the magnitude measured, S, while in the case of direct analysis, the two magnitudes are proportional to one another, and have, therefore, the same degree of accuracy. In other words, if in the determination of potassium as potassium platinochloride, an error of $\frac{1}{100}$th is made in the weight of this compound, the amount of potassium calculated from it will also be wrong to the extent of $\frac{1}{100}$th. If, however, an error of $\frac{1}{100}$th is made in the determination of S, the error in the calculation of x will be greater. In the first example, it amounts to 4 per cent, in the second to more than 20 per cent, of which one can easily convince oneself by performing the calculation. This is due to the fact that the magnitude sought, x, is proportional not to the measured value, S, but to the difference $S-k$, as the formula shows. If, for example, k is half as great as S, an error of one hundredth in S will be equal to an error of two hundredths in $S-k$, and, accordingly, the determination

of x will be erroneous to the extent of two hundredths of its value. In general, the relative error in the result is to that in S as S is to $S - k$, and it becomes all the greater the smaller the differences $S - k$.

* The practical rules for the choice of indirect methods, which can be deduced from the above, will not be given here; on the contrary, it may be left to the student to think these out.

Sodium Hydroxide.—The properties of this important compound have already been described; along with caustic potash, it forms the type of a strong base.

Towards water, caustic soda behaves in the same way as caustic potash; it dissolves with great evolution of heat to form a very concentrated solution, from which a hydrate $2NaOH + 7H_2O$ separates out in the cold. On evaporation by boiling, the solution passes, as in the case of caustic potash, into the fused, anhydrous compound; the reason of this behaviour, which differs from that which is usual in the case of solutions of solid substances, is the same as in the case of caustic potash. In moist air caustic soda takes up water and deliquesces, but it resolidifies again by absorption of carbonic acid much more quickly than deliquesced caustic potash, because the normal sodium carbonate is not deliquescent and is deposited in the solid state.

For the preparation of caustic soda, the methods given on p. 445 can be repeated almost word for word. It is now obtained by electrolysis from sodium chloride or common salt, whereas, formerly, it was almost exclusively obtained by the decomposition of sodium carbonate with lime.

If it is a question of obtaining small quantities of sodium hydroxide for laboratory purposes, we may start with metallic sodium and decompose this with water. One of the simplest methods of preparing it is to place metallic sodium (best in the form of wire or of ribbon) in a dish of platinum or of silver standing in a desiccator containing water. The sodium decomposes the water vapour and is converted into caustic soda, while the hydrogen escapes. The desiccator must, therefore, be furnished with a tube which allows the hydrogen to pass out without allowing the atmospheric carbonic acid to enter. For this purpose a tube filled with soda lime, *i.e.* a mixture of caustic soda and lime, is used.

It can also be prepared by pouring water over sodium amalgam. The decomposition of the latter takes place slowly and with moderation, especially after some caustic soda has been formed, and a dilute solution of very pure caustic soda is thus obtained. If it is desired to have it free from carbonic acid, care must be taken that the carbonic acid which is usually present in distilled water is previously removed.

Lastly, a very pure solution of caustic soda can be obtained by the decomposition of sodium sulphate solution with barium hydroxide. The small quantities of the latter which dissolve in the soda solution are removed by the addition of the necessary amount of sodium sulphate solution.

In the decomposition of water by sodium, a considerable amount of heat, viz. 183 *kj*, is evolved. From the corresponding equation of reaction, the heat of formation of dissolved caustic soda is found to be 468 *kj*. Since in the neutralisation of caustic soda with a strong acid further 57 *kj* are evolved (p. 200), the heat of solution of sodium in such an acid is greater by this amount than in water, viz. 240 *kj*. According to the statements made on p. 201, the same number gives the heat of formation of sodion from the metal, so that we have the equation $Na + aq. = Na^{\cdot} aq. + 240$ *kj*. This value is somewhat less than for potassium, but the difference is slight.

By adding the heat of formation of sodion, 240 *kj*, to that of any anion, the heat of formation of the corresponding salt in aqueous solution is obtained.

As in the case of caustic potash, the reactions of caustic soda are chiefly due to hydroxidion; to this extent, therefore, they are identical with those of caustic potash. As a matter of fact, both hydroxides are used in the laboratory without distinction so long as we are dealing with hydroxidion reactions, *i.e.* with the action of basic properties. This is also the case in the arts; in this case, the price alone determines the choice. Formerly, caustic soda was considerably cheaper than caustic potash, but at the present time the difference is less.

Sodium Peroxide.—If sodium is heated in dry air it burns to a heavy, yellowish powder, the composition of which is represented by the formula NaO or Na_2O_2. With regard to the molar weight of this substance, nothing is known; on account of its relation to hydrogen peroxide, the formula Na_2O_2 has a certain amount of probability.

This compound, which is called *sodium peroxide*, dissolves in water, yielding a liquid with alkaline reaction which exhibits the reactions of hydrogen peroxide.

Dissolution, however, without decomposition can scarcely be effected; usually a certain amount of oxygen, depending on the conditions of experiment, is evolved at the same time; the amount is all the smaller, the more local heating is avoided.

It may therefore be assumed that the reaction can be expressed for the most part by the equation $Na_2O_2 + 2H_2O = H_2O_2 + 2NaOH$. The two substances, caustic soda and hydrogen peroxide, do not, however, exist together independently, but chemical union takes place which probably leads to the formation of a certain amount of sodium peroxide. This amount will be dependent on the temperature and the concentration; with regard to its actual amount there are no exact determinations.

The solution of sodium peroxide is used for oxidation purposes in place of hydrogen peroxide, especially in the bleaching of textile goods. The compound is, therefore, prepared on a large scale by exposing sodium in vessels of aluminium to the action of dry air free from carbonic acid. By suitable arrangements, based on the principle of counter-currents, too great an elevation of temperature, by which the vessels would suffer, is avoided.

In the dry state, also, sodium peroxide acts as a very powerful oxidising agent. In contact with it, carbonaceous substances readily ignite spontaneously, so that in working with it the presence of organic substances must be avoided.

The excess of energy which is present in sodium peroxide can be used for obtaining metallic sodium by instituting a suitable "coupled" reaction (p. 203). If the substance is mixed with rather more than a tenth of its weight of dry charcoal and heated, a violent reaction occurs whereby sodium carbonate is formed and metallic sodium distils over: $3Na_2O_2 + 2C = 2Na_2CO_3 + 2Na$. This is one of the simplest methods of showing on a small scale the formation of metallic sodium from one of its compounds.

Sodium Chloride.—The most widely distributed of all the sodium salts is the chloride, which, as common salt, is the type of the salts. In nature it occurs both in the solid state, as rock-salt, and in solution. The water of the ocean, more especially, contains as chief secondary constituents, chloridion and sodion, *i.e.* common salt. The concentration of the dissolved sodium chloride differs somewhat in the different seas; in the Baltic Sea it is very small, in the Mediterranean it is comparatively great. This depends on the relation between the inflow of water and the loss by evaporation. If the inflow of the rivers, which contain much less sodium chloride than the water of the sea, exceeds the evaporation, a more dilute solution is produced; this is the case in the Baltic Sea. On the other hand, if the evaporation preponderates, the remaining liquid becomes more and more concentrated. This is the case to a certain extent in the Mediterranean; a specially good example of this state of matters is furnished by the Dead Sea, in which the salt concentration approaches almost to saturation.

The average amounts of salt contained in 100 parts of sea-water are:—

Dead Sea	22·0
Mediterranean	3·8
Atlantic Ocean	3·6
Baltic Sea	0·5

Where the evaporation greatly predominates, the common salt is ultimately deposited in the crystalline state, and forms beds of rock-salt. This salt is frequently not pure, but is mixed with other substances which were present in the water.

If the water which flows through the soil comes into contact with strata containing salt, it dissolves the latter and then appears as "salt springs." From these, the sodium chloride is obtained by evaporating the water. In order to save a part of the firing, the brine is allowed to trickle over high stacks of brushwood in order that as large a portion as possible of the water may be removed by free evaporation in the air. Since the brine thereby increases in concentration (which is measured in "degrees" (Lat. *gradus*) of the hydrometer), this process is called "graduation." In this way the concentration can be increased only to a limited amount, since the vapour pressure of the salt solution diminishes as the solution becomes more concentrated. As is evident the result also depends on the relative humidity of the air.

In ordinary circumstances, sodium chloride crystallises in colourless and transparent cubes belonging to the regular system. Chance colorations of rock-salt often occur owing to impurities; a red coloration, produced by oxide of iron, is especially frequent.

The density of pure sodium chloride amounts to 2·15. The refraction and dispersion of light are small. A special property of rock-salt is its transparency for rays of long wave length lying beyond the red. By reason of this behaviour, it differs greatly from other substances. Whereas glass, for example, is just as permeable for the *visible* rays as rock-salt is, and appears, therefore, just as transparent, it behaves as an opaque substance towards rays of long wave length, and absorbs them, converting them into heat.

At 775° sodium chloride melts, and at the same time it begins to volatilise appreciably.

In water, sodium chloride readily dissolves. At room temperature, the saturated solution contains 36 parts of salt to 100 parts of water, and at the temperature of boiling, 39 parts of salt, or only a little more. It has already been described (p. 462) how this property is made use of in the separation of common salt from other salts whose solubility changes greatly with the temperature.

The solution of sodium chloride exhibits the reactions of chloridion and of sodion. It has a pure saline taste, and the higher animals all experience the need of taking in larger or smaller amounts of common salt with their food. This is seen most markedly in the case of the herbivora. Localities where common salt can be obtained are eagerly sought out, often at the risk of their life, by stags, roe-deer, and similar animals. Carnivorous animals exhibit a much less desire for salt. This is connected with the fact that with the vegetable food relatively large amounts of potassium salts are introduced into the body, whereby the secretion of sodium is greatly promoted and a necessity for its replacement caused. In the case of animal food, however, the two elements are taken up in the proportions proper to the animal organism.

In the case of the vertebrate animals, the sodium compounds occur chiefly in the blood plasma and in the fluids of the body, while the potassium, as already mentioned, collects in the blood corpuscles.

From aqueous solutions of sodium chloride the well-known cubical crystals of the anhydrous salt separate out at temperatures above − 2°. Owing to the usually bad formation of these crystals, they enclose some mother liquor, so that when heated they give off small amounts of water. On being heated, the enclosed water is converted into vapour, the pressure of which increases as the temperature rises until it becomes so great that the pieces of salt enclosing the liquid are shattered, whereby a crackling noise is produced. Having once undergone this treatment, the salt remains quiet on being again heated.

From concentrated solutions of sodium chloride at lower temperatures, a hydrated salt of the formula $NaCl + 2H_2O$ separates out in monoclinic crystals. These are stable only up to − 2°; if heated above this temperature, they melt and form a liquid from which the anhydrous salt immediately separates out in the form of small cubes.

* Even at the room temperature, these hydrated crystals are produced as an unstable form, when a solution of common salt is spread out in a thin layer on a glass plate and caused to evaporate rapidly by blowing on it. Under these circumstances, the separation of oblique crystals can be observed with a low power of the microscope; in a short time the ordinary cubes of common salt appear here and there, and these absorb the former crystals.

Common salt is used not only in food, but, being the most widely distributed salt of sodium, it is used as the starting-point in the preparation of metallic sodium and of all other sodium compounds. Some of its transformations have already been mentioned; others will be discussed presently.

Sodium Bromide and **Sodium Iodide** are similar to sodium chloride, only more soluble than the latter. At lower temperatures, both form hydrated crystals with $2H_2O$ of crystallisation, isomorphous with those of the hydrated sodium chloride. The temperature, however, at which they melt and pass into the anhydrous salts and the saturated solution of these, is higher. In the case of sodium bromide the conversion takes place at 50°, in the case of sodium iodide at 67°.

On investigating the solubility of these salts in water, and its change with the temperature, the relations are found which are represented in Fig. 107. The curve marked $NaBr + 2H_2O$ refers to the hydrated sodium bromide, that marked $NaBr$ to the anhydrous salt. Similarly for the two forms of sodium iodide. As can be seen, each of the two forms has its own solubility curve, which is independent of the other. The point where the two curves cut is the point where the two forms can exist along with the saturated solution. This is the same temperature at which the hydrated crystals commence to melt.

From this it follows that each form of the salt has its own solubility, and that the two forms have the same solubility at the temperature at which they change into one another. In this respect, therefore, salts with different amounts of water of crystallisation behave like the different forms of allotropic substances (p. 259).

As the diagram shows, the solubility curves are both produced beyond the point of intersection. This signifies that the transition does not necessarily occur here any more than in the case of the transition of allotropic forms, but that on both sides there may be supersaturation. An examination of the diagram also teaches that the less stable form has always a greater solubility than the more stable, so that a solution saturated in respect of the unstable form, on being brought into contact with "nuclei," *i.e.* already formed crystals, of the stable form, will deposit solid salt in this form ; the solution is, therefore, supersaturated with respect to this form.

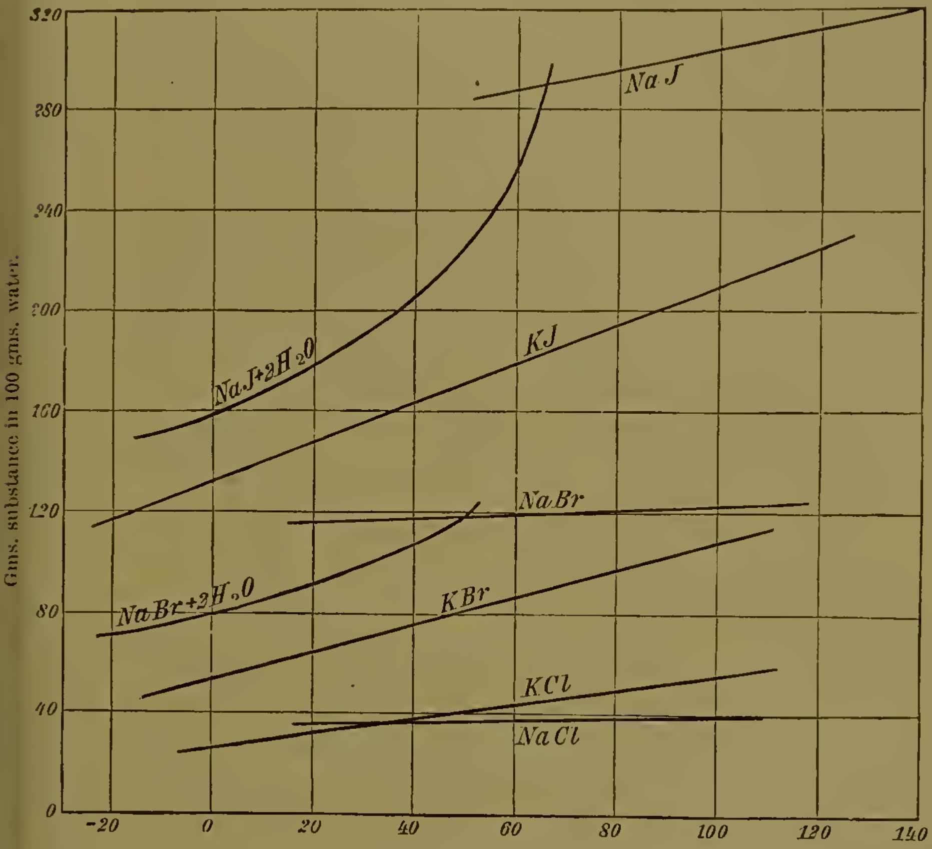

FIG. 107.

If, for example, a saturated solution of anhydrous sodium bromide is made at 30°, and crystals of the hydrated salt are introduced into it, the latter will grow and the residual solution will exhibit the smaller concentration which belongs to this form. On the other hand, a solution of the hydrated salt, saturated at 30°, will be found to be unsaturated with respect to the anhydrous salt, *i.e.* it will be able to dissolve certain quantities of this salt. The presence of the hydrated salt must, however, be most carefully avoided, for excessively small quantities of this are sufficient to cause the separation of that form. If, however, the anhydrous salt is heated immediately before the experiment, all hydrated salt is destroyed, and the salt can be dissolved without fear.

The above discussion holds universally. It shows that we may speak of the solubility of a salt or, generally, of a solid substance, only when we state the form which is in equilibrim with the solution. In general, every form has its own solubility, and the point at which the solubility of the two forms becomes equal, is the transition point of the one form into the other.

Conversely, every curve representing the change of solubility with the temperature is, for each form, continuous. If a break in the solubility curve is observed, this is a certain proof that the solid substance which is in equilibrium with the solution has passed into another form at the temperature of the break.

Sodium Bromate.—The pure compound is of no special interest. Mixed with sodium bromide, in which condition the salt is obtained from bromine and caustic soda ($6NaOH + 3Br_2 = NaBrO_3 + 5NaBr + 3H_2O$), it constitutes a reagent which is used for liberating a known quantity of bromine in solution. On acidifying the mixture, the same amount of bromine is set free as was used in the preparation of the mixture. The reaction can be expressed by the equation $HBrO_3 + 5HBr = 3H_2O + 3Br_2$, or, writing the ions, $BrO_3' + 5Br' + 6H^{\cdot} = 3H_2O + 3Br_2$. The mixture is obtained by adding bromine to caustic soda until the colour of the former is permanent, and then evaporating the solution; the excess of bromine is hereby driven off.

Sodium Chlorate.—In contradistinction to potassium chlorate, sodium chlorate is a salt which is very abundantly soluble in water. At the present time, therefore, when the method of preparing it on a manufacturing scale has become known, this salt is employed in many cases in which chloranion is used on account of its oxidising action, and where a more concentrated solution is desired than can be attained with potassium chlorate. It is obtained in a similar manner to potassium chlorate. It forms finely crystallised cubes and other forms of the regular system, and these have the property of rotating the plane of polarised light in a manner similar to quartz. Whereas, however, the latter exhibits this phenomenon in a regular manner only when the light passes through the crystal parallel to the chief axis, sodium chlorate rotates the plane of polarised light by equal amounts, no matter what the direction of the ray in the crystal is. This is a consequence of the fact that these crystals belong to the regular system, while those of quartz are hexagonal.

Sodium Nitrate.—This salt, which crystallises anhydrous in large rhombohedra, melting at 320°, is, at the present day, the most important of the compounds of nitric acid. It is found in large quantities in Chili. Since no rain falls in those districts, it has been possible for this salt to be preserved. How it has been formed can, as yet, not be stated with certainty or probability; the constant presence in it of iodine compounds in the form of sodium iodate, speaks in favour of its formation from the salts of sea-water. It is, however, still a mystery what conditions existed to produce such a powerfully oxidising effect that, along with the nitrate, the iodine should have passed into the iodate, and even a portion of the chlorine into perchlorate (which is also found in Chili saltpetre under certain circumstances to the extent of several per cent). We may, perhaps, suppose that at the time of the formation of this salt some cause was active by which unusually large amounts of ozone were produced; the action of this would render the formation of these highly oxidised substances from any sodium compounds present, intelligible.

The crude sodium nitrate is mixed with earth and clay, and is purified by a simple process of crystallisation. The purification can be easily and successfully carried out by this method, since the solubility of this salt changes very greatly with the temperature, as can be seen from the following table:—

Solubility of Sodium Nitrate.

Temperature.	100 gm. water dissolve—
− 6°	68·8 gm. of $NaNO_3$
0°	72·9 ,,
+ 20°	87·5 ,,
40°	102 ,,
60°	122 ,,
80°	148 ,,
100°	180 ,,
110°	200 ,,

Sodium nitrate is used in large quantities for manuring purposes; it forms the most important artificial nitrogen manure for cultivated plants, and its application is limited only by the price. The nitrogen is most easily available for the plant in the form of nitranion, and this manure has, therefore, the quickest action. Since, however, the soil does not retain this substance, as it does potash, phosphoric acid, and ammonia, the manuring with Chili saltpetre must be carried out immediately before the time when the plant requires the nitrogen.

Sodium nitrate is further used in large quantities for the preparation of nitric acid (p. 318) and for conversion into potassium nitrate (p. 462). It is also used in the preparation of nitro-compounds; for this purpose, the nitric acid is not first prepared from the salt, but a mixture of sodium nitrate and sulphuric acid, which on distillation would give nitric acid, is directly employed. Lastly, a considerable portion of the salt is converted into sodium nitrite, which is employed n enormous quantities in the preparation of artificial dyes.

Sodium nitrate cannot be used in place of potassium nitrate for the preparation of gunpowder and blasting powder, because the powders made from it become moist.

Sodium Nitrite.—At the present day, sodium nitrite is manufactured and used in large quantities in place of potassium nitrite, from which it differs in the ease with which it can be prepared pure. It is a very soluble salt with a feebly alkaline reaction; when treated with acids, it evolves red fumes of the oxides of nitrogen (p. 329). It is obtained, similarly to potassium nitrite (p. 464), by heating sodium nitrate with metallic lead.

Sodium Sulphate.—The normal sodium sulphate, Na_2SO_4, is well known in the form of hydrated crystals of the composition $Na_2SO_4 + 10H_2O$, by the name of Glauber's salt. It received its name from Glauber (born about the year 1640), a physician and chemist, who introduced it as a drug; he ascribed to it great healing power, and gave it the name "sal mirabile." Its action on the human organism consists essentially in the fact, that when it gets into the intestines, it makes their contents more watery and thereby facilitates the evacuation.

* This action arises from the fact that the walls of the intestines offer considerable hindrance to the diffusion of Glauber's salt. The equalisation of concentrations, the tendency towards which is exerted under all circumstances, cannot, in this case, be accomplished by the dissolved substance mixing with the body fluids, but, on the contrary, water must pass from the latter into the intestine.

* From this it follows that all other salts which have the same property of not passing through the intestinal walls, and which do not exert any other actions on the organism, must also behave in the same way. This is, indeed, the case; magnesium sulphate (Epsom salts) acts in exactly the same way as Glauber's salt.

The solubility relations of sodium sulphate are rather complicated, and are represented in Fig. 108. Three different solubility curves can be distinguished, belonging to three different forms of the salt. Of these forms, one, stable at higher temperatures, is anhydrous; at medium temperatures, ordinary Glauber's salt with $10H_2O$ of crystallisation, is stable; besides these, an unstable salt can be obtained at lower temperatures containing $7H_2O$ of crystallisation.

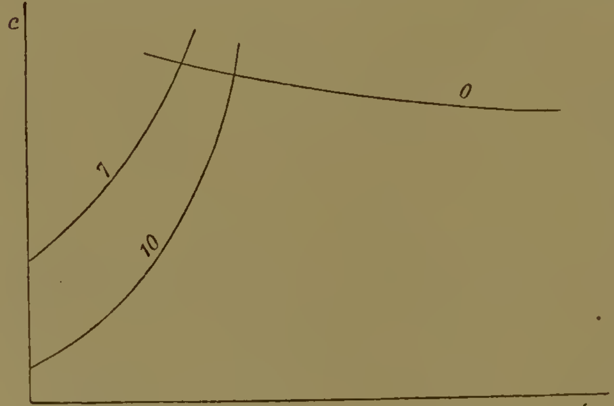

Fig. 108.

On following the curves in Fig. 108 from right to left, we have, in the first place, the curve of the anhydrous salt, marked *o*, which, in contrast with the behaviour of most salts, ascends as it passes in the direction of lower temperatures. The fact that the solubility of the salt diminishes with rising temperature, is connected with the other fact that the salt dissolves in its almost saturated solution, with evolution of heat, or, absorption of heat occurs when it separates out from a supersaturated solution (p. 216).

The curve of the anhydrous salt can be followed downwards to about 20°. From 32° downwards, however, the solutions are supersaturated with respect of the ordinary Glauber's salt with $10H_2O$, and they can therefore be obtained only when the presence of this latter salt is strictly avoided. This requires some care; for, as we shall see presently, the salt is everywhere present in dust.

At 32°, the curve of the anhydrous salt is cut by the solubility curve of Glauber's salt (marked with 10); at this point, therefore, both salts can exist along with the solution, since at this point the saturated solutions contain the same amount of salt. This state is most easily obtained by heating Glauber's salt to 32°. It appears then to undergo fusion. We are here dealing, however, with a more complicated process, for the liquid does not have the same composition as the solid Glauber's salt, but contains more water. This is due to the fact that anhydrous salt separates out at the same time; for this reason, the salt does not pass into a clear liquid, no matter how long it is heated, but forms, after the Glauber's salt has disappeared, a paste of anhydrous salt and saturated solution.

The solubility curve of Glauber's salt with $10H_2O$, can be followed downwards to somewhat below 0°. The solubility of the salt diminishes very rapidly as the temperature falls, so that at 0° the liquid contains only 0·05 of sodium sulphate (calculated as anhydrous salt).

So far as we have yet considered the relations, we are dealing with two independent solubility curves, of which the one belongs to the anhydrous salt, the other to the salt with $10H_2O$. The present case is distinguished from that of sodium bromide and sodium iodide only by the fact that one of the curves slopes downwards, while in the case of the latter salts, both curves slope upwards.

It has to be specially noted that the break in the solubility curve at 32° is due solely to the fact that the *solid phase* in the solution equilibrium changes at this temperature. It was formerly thought that something special took place in the solution at this temperature, such as, say, that below 32° the salt was dissolved in a hydrated form, above that temperature, in an anhydrous form; even now, such unfounded views are sometimes met with. However, on investigating the properties of the *solution* at its passage through this point, no sort of break was found, and so far as the solution is concerned, this temperature is in no way distinguished from other temperatures. The only thing that changes at this temperature is the nature of the *solid* salt, and this is the all-sufficient reason for the occurrence of the new solubility curve.

The phenomena, now, become somewhat more complicated from the fact that solutions can be fairly easily prepared which are considerably supersaturated with respect to the salt with $10H_2O$. Indeed, the phenomenon of supersaturation has in no case been studied more fully than in the case of Glauber's salt.

Such supersaturated solutions are obtained by heating Glauber's salt with half its weight of water until all solid particles have disappeared, closing the vessel and allowing it to cool down. The stopper does not require to be air-tight but only dust-tight; a plug of cotton-wool, for example, is therefore sufficient. If this is removed, after the solution has cooled down, crystallisation, as a rule, commences at once. This is due to the fact that Glauber's salt is extremely widely distributed in the dust of towns, being formed from the compounds of sodium everywhere present (p. 472), and the sulphurous acid which is produced in the combustion of coal, and is derived from the sulphur therein contained. If the experiment is carried out in the country far from such sources of dust containing Glauber's salt, the crystallisation can also be excluded. Since it was for long not believed that this was the cause of the "spontaneous" crystallisation of Glauber's salt, the crystallisation of the supersaturated solution appeared as something peculiar and mysterious. By working with other substances, however, which do not, or only rarely, occur in the dust, one can convince oneself that in general supersaturated solutions possess a great stability, and that it is only towards nuclei of their own solid substance that they are unstable.

* The amounts of solid substance which give rise to crystallisation, are small but not immeasurably so. The limit lies about one millionth of a milligram.

On cooling down a supersaturated solution of Glauber's salt to about 5°, other crystals make their appearance, which have the composition $Na_2SO_4 + 7H_2O$, and whose solubility curve is also given in Fig. 108. Throughout its whole course, this curve lies above the curve of the salt with $10H_2O$, from which it follows that the solutions saturated with the salt 7, are always supersaturated with respect to the salt 10. If, therefore, some of the salt 10 is introduced into a system composed of salt 7 along with solution, the solution will, in the first place, deposit salt until the point of saturation with respect of 10 is reached, *i.e.* the concentration of the solution will reach that point on the curve 10 which lies below the former point on curve 7. Such a solution, however, is unsaturated with respect to 7; consequently, this salt must dissolve. The solution thereby again becomes supersaturated with respect to 10, and this separates out. This evidently goes on until, finally, all the salt 7 has disappeared and is replaced by 10.

It may be asked, why does the unstable salt 7 separate out first at all, since, of course, the solution could give the stable salt 10 directly. The answer is to be found in the universal rule that the less stable forms first appear (p. 207).

Finally, if the solution be cooled down to about – 15°, Glauber's salt separates out spontaneously from it and supersaturation ceases, and this too without a nucleus of the solid salt being necessary. The region in which the separation does not occur without such a nucleus, can be distinguished as the *metastable region*, from that region, the *unstable region*, in which separation takes place without a nucleus. Every case of supersaturation leads, in the first place, into the metastable region, and from this then into the unstable. The limits of the two regions are, however, difficult to fix.

The crystals of Glauber's salt *effloresce* in the air, *i.e.* they lose water and become converted into a fine white powder of anhydrous salt. The cause of this is that the vapour pressure of Glauber's salt (or, more exactly, of a mixture of Glauber's salt and anhydrous salt) is greater than the mean vapour pressure of the water in the air (p. 122), so that the salt must lose water and pass into anhydrous salt.

* On the basis of this remark, the objection may be made to the explanation of the crystallisation of supersaturated solutions of Glauber's salt by dust, that according to the above statement there can be no Glauber's salt present in the dust, but only effloresced Glauber's salt, *i.e.* anhydrous salt. This is so; nevertheless, experiment shows that even effloresced Glauber's salt can also effect the crystallisation of the supersaturated solutions, and loses this property only when it has been heated. In the effloresced salt at the ordinary temperature, then, there are apparently sufficient traces of unchanged Glauber's salt present to bring about crystallisation. Or, there is produced on efflorescence, a form of the salt which in contact with the solution immediately gives Glauber's salt, a behaviour which the anhydrous salt certainly does not show, after it has been heated. Which of these two possibilities corresponds to the truth, has not yet been determined.

Intact crystals of Glauber's salt can be kept in dry air without efflorescing; if, however, efflorescence has once begun at any point, it spreads out from that point, and this it does in accordance with a law which is determined by the crystalline form of the efflorescing salt (p. 265). We have here again a phenomenon of the nature of supersaturation, which can be removed only by the presence of a further phase. Applying the phase law to this case, we obtain the following: Since the given system consists of two components, sodium sulphate and water, the sum of phases and degrees of freedom is 4. If hydrated salt and water vapour are given as two phases, the system has still *two* degrees of freedom, *i.e.* at a given temperature, every value of the vapour pressure (within certain limits) can exist. If, however, another phase is added, only one degree of freedom remains, *i.e.* to every temperature there belongs a definite pressure. Such a system, therefore, behaves as a pure liquid, for it has a definite vapour pressure which is independent of the amounts of the phases, *i.e.* independent of the relative quantities of Glauber's salt, anhydrous salt, and water vapour. Observation shows that such a law does indeed hold, but this pressure is established more slowly than in the case of a liquid.

Since *both* solid phases are required for the definition of the system just considered, it follows that one cannot speak simply of the vapour pressure of a hydrate; on the contrary, it must be stated what other solid substance is also in equilibrium with the vapour. Many salts form several hydrates; every combination, therefore, of two hydrates (or of a hydrate and the anhydride) must have its own vapour pressure. This also has been confirmed by experiment.

Besides being used for medicinal purposes, sodium sulphate is also employed as such in the manufacture of glass and in some other industries. It occurs as a by-product, and as an intermediate product in much larger quantities. As a by-product, it is obtained in the preparation of hydrochloric acid from common salt, and of nitric acid from sodium nitrate. The greater part of the salt is converted into sodium carbonate or soda. The methods by which this is accomplished, will be discussed immediately.

Sodium sulphate also occurs in nature. As a mineral, it is called thenardite. It is a very frequent constituent of the natural waters; waters which contain large quantities of this salt in solution, such as the Carlsbad waters, are used as mineral waters for the removal of disturbances of the nutrition.

Acid Sodium Sulphate.—This salt is prepared in the same manner as the corresponding potassium salt, is used for the same purposes, and exhibits the same chemical relations.

Sodium Sulphite.—The normal salt of the composition $Na_2SO_3 - 7H_2O$, occurs in commerce in large crystals; it is chiefly used in photography for adding to the "developers" to preserve these against the oxygen of the air. The developers are alkaline solutions of various organic compounds, the purpose of which is to reduce the silver compounds of the exposed photographic plate to metallic silver. Sodium sulphite, it is true, scarcely possesses the power to effect this reduction, but it prevents to a certain degree the oxidation of the developer in the air, and so keeps this for a longer time uncoloured and fit to be used.

The salt dissolves readily in water. On being heated, it decomposes, similarly to sodium sulphate, into anhydrous salt and a saturated solution; its solubility exhibits corresponding changes.

When exposed to the air, the crystals soon become covered with a coating of powdery sodium sulphate, which is formed by the oxidation of the salt. It can be seen, therefore, from the appearance of the salt, whether it is still fit to be used or not.

Acid sodium sulphite, $NaHSO_3$, is also known. It is deliquescent, and oxidises in the air still more readily that the normal salt. Its concentrated solution is used in the arts.

The oxidation of solutions of this salt in air is very greatly retarded by the presence of organic substances, such as alcohol or sugar. Here again we are dealing with a case of catalytic influence, which, however, produces not an acceleration but a retardation of the reaction. The accelerating catalysers can be distinguished as positive from the retarding or negative catalysers.

Sodium Sulphide.—With regard to the behaviour of the aqueous solutions of sodium sulphide, Na_2S, and of sodium hydrosulphide, NaHS, the reader may be referred to what was stated in the case of potassium sulphide (p. 460). With regard, however, to the solid salts, it may be mentioned that from solutions of sodium sulphide, well formed crystals belonging to the quadratic system, and containing $9H_2O$ of crystallisation, can be obtained. Anhydrous sodium sulphide is obtained as a flesh-coloured mass by the reduction of sodium sulphate with charcoal.

Impure mixtures of various polysulphides of sodium, along with sodium sulphate or sodium thiosulphate (according to the temperature employed), which are prepared under the name of liver of sulphur by fusing together soda and sulphur, are used in medicine and in various industries.

Sodium Thiosulphate is the best known salt of thiosulphanion (p. 295). It is obtained by warming solutions of normal sodium sulphite with sulphur; the latter is dissolved, and the solution then contains the salt $Na_2S_2O_3$, the composition of which differs from that of the sulphite only by one combining weight of sulphur. From the solution it is obtained by evaporation in the form of large, transparent crystals of the monoclinic system containing $5H_2O$ of crystallisation.

In the manufactures, sodium thiosulphate is prepared from the calcium sulphide of the "soda-waste" (p. 491); by oxidation in the air, this is converted into calcium thiosulphate, which is then transformed into the sodium salt by means of sodium sulphate.

The salt is used in large quantities. To a certain extent it is used in photography for "fixing." It has the property of dissolving difficultly soluble salts of silver, and pictures which have been produced from these are treated with this salt in order to remove the unchanged silver salt, and to render the pictures unchangeable by light. The theory of these processes will be given under silver.

Further, large quantities of thiosulphate are used as an "antichlor" for the purpose of removing the last traces of free chlorine from the fibres of material which has been bleached by its means. Free chlorine is converted by this salt into chloridion, which is harmless; at the same time, sulphuric acid is formed. The reaction can be written: $Na_2S_2O_3 + 4Cl_2 + 5H_2O = 2NaCl + 2H_2SO_4 + 6HCl$.

Bromine acts similarly to chlorine. Iodine, on the other hand, converts the thiosulphate only into tetrathionate. Since the reaction has already been discussed on a former occasion (pp. 297 and 300), we shall only repeat the equation here: $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$, or, writing the ions, $2S_2O_3'' + I_2 = S_4O_6'' + 2I'$.

Sodium thiosulphate is used, therefore, in volumetric analysis for the determination of free iodine. For this purpose, it possesses the very important advantage that its solutions keep perfectly in the air and are not oxidised. In this respect it is greatly superior to sodium sulphite, which was formerly used for the same purpose. Care, only, must be taken that the solution of thiosulphate does not become acid; in very dilute solutions, even the carbonic acid of the air effects the decomposition described on p. 295, with deposition of sulphur. Since the iodine reaction is very sensitive, it is just here that one preferably uses dilute solutions; these must, therefore, be prepared shortly before being used. This is best done by diluting a measured amount of a concentrated stock solution (*e.g.* a normal solution) which remains unchanged for a long time. Such a normal solution contains, in accordance with the above reaction equation, one mole or 248·34 gm. of the crystallised salt $Na_2S_2O_3 + 5H_2O$ in a litre.

If a solution of sodium thiosulphate is added to a solution containing iodine, which may be neutral or acid, a corresponding amount of the free iodine disappears; the complete disappearance can be readily recognised by adding some dissolved starch and titrating till the blue colour of the starch iodide disappears.

This volumetric method is not limited to the determination of free iodine, but can, evidently, be applied to all substances which either form iodidion from iodine or, conversely, convert iodidion into free iodine. To the latter belong most of the oxidising agents; to the former, many reducing agents. Thus, free chlorine or bromine as well as chloric acid, hypochlorous acid, iodic acid, etc., can be titrated, by adding to them an excess of potassium iodide and determining the amount of iodine liberated by means of thiosulphate. As an example, we shall describe the determination of potassium iodate. In acid solution, this reacts with potassium iodide according to the equation $KIO_3 + 5KI + 6HCl = 6KCl + 3I_2 + 3H_2O$, or, written in ionic form, $IO_3' + 5I' + 6H^{\cdot} = 3H_2O + 3I_2$. For every mole of iodanion, six combining weights of free iodine are formed, and, therefore, six moles of sodium thiosulphate are used.

Reducing substances can be determined by bringing them together with a measured excess of free iodine (dissolved in potassium iodide), and titrating the amount of iodine remaining after the reaction, with thiosulphate.

For some reactions it is of importance to notice that in the interaction of iodine and thiosulphate, the alkali titre of the solution does not change. In other words, hydrion is neither used up nor formed in this reaction.

If the crystallised salt is heated to 56°, it melts without leaving a solid residue; it behaves, therefore, differently from sodium sulphate or sodium sulphite. The fused salt may be allowed to cool without its solidifying; if, however, a particle of the solid salt is introduced, crystallisation commences at once. This fused substance is especially good for showing that crystallisation is effected only by the presence of the solid salt, and does not consist, say, in a disturbance of "the unstable equilibrium of the atoms." Thus, if a glass rod whose end is covered with a firmly adhering coating of the salt (all loose particles must be carefully removed) is introduced into a fairly large amount of the cooled fused thiosulphate, crystallisation proceeds solely from the rod outwards, and after a few seconds the glass rod with the bunch of crystals adhering to it can be removed from the liquid, without this continuing to crystallise.

Sodium Carbonate.—Normal sodium carbonate, Na_2CO_3, is a white salt which readily dissolves in water with alkaline reaction; when anhydrous it melts at 850°, and can unite with water to form various hydrated compounds.

Besides the anhydrous salt, at least four hydrates are known with certainty. By boiling down a hot saturated solution, a salt of the formula $Na_2CO_3 + H_2O$ is deposited. If the solution is allowed to cool down in the air, the ordinary crystallised salt containing $10H_2O$ is obtained. On cooling down the hot saturated solution, with exclusion of dust, two different salts are obtained, both of which contain $7H_2O$ but have a different crystalline form and also a different solubility. Which of the two is formed, depends essentially on the concentration of the solution.

Besides these salts, other hydrates with 3, 5, and 15 molecules of water of crystallisation have been described.

Each of these hydrates has its own solubility, and the different solubility curves cut one another in a manner similar to that described in the case of Glauber's salt. The most stable forms are those with $10H_2O$ and with $1H_2O$; these two behave to one another essentially as Glauber's salt and anhydrous sodium sulphate. The two salts are also similar in the fact that the solubility of the form which is stable at higher temperatures diminishes as the temperature rises. The transition point of the salt with $10H_2O$ into that with $1H_2O$ and saturated solution, is 34°; at that temperature, therefore, sodium carbonate is most abundantly soluble in water.

The acid salt, or *sodium bicarbonate*, $NaHCO_3$, crystallises anhydrous, and is much less soluble than the normal carbonate; for 100 parts of water dissolve only 9 parts of salt at 12°, and 10 parts at 22°. On being heated, or when its aqueous solutions are boiled, it readily parts with carbon dioxide (cf. potassium bicarbonate, p. 457).

Besides these two salts, double salts of the two are also known, some of which occur in nature (trona and urao). The composition is represented by the formula $HNa_3C_2O_6 + 2H_2O$. As naturally occurring soda they were formerly of importance in the arts; their amount, however, in comparison with the consumption, is very scant.

Normal sodium carbonate, under the name of soda, is one of the longest known salts. It was formerly obtained from the ash of sea plants rich in soda in the same manner as potashes from the ash of land plants containing potash, and it was employed for essentially the same purposes as potashes, viz. for the preparation of soap and of glass. The rapidly increasing demand for these substances and the simultaneous replacement of wood fuel by fossil fuel, the ash of which contains no alkali carbonates, rendered it necessary to discover other sources of these substances.

In certain localities, it is true, sodium carbonate occurs partly in the solid state as an efflorescence on the soil, partly dissolved in water of springs and lakes; but the quantities thus available are quite insufficient to supply the great demand.

Since the beginning of the nineteenth century, therefore, sodium carbonate has been artificially prepared from the most widespread sodium salt, viz. sodium chloride. The process given by Le Blanc, which was for a long time the one exclusively employed, is now replaced by other methods, chemical as well as electrolytic.

The method of Le Blanc is rather troublesome. The sodium chloride is first converted into sodium sulphate with sulphuric acid, this is heated with charcoal in order to reduce it to sodium sulphide, and, lastly, this is strongly heated with calcium carbonate, sodium carbonate and calcium sulphide being thereby formed. These two salts are separated by extracting with water, in which the calcium sulphide is very difficultly soluble.

Expressed in equations, these reactions are:—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$
$$Na_2SO_4 + 4C = Na_2S + 4CO$$
$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The second and third processes are carried out in one operation, the sodium sulphate being mixed with coal and limestone, and the mixture heated.

Since in this process very large quantities of sulphuric acid are used up and correspondingly large amounts of hydrochloric acid are obtained, a soda works which employs the method of Le Blanc is necessarily carried on in conjunction with a sulphuric acid works; to this a plant is also added for converting the hydrochloric acid, for which there is no market to the extent in which it is formed, into other products, generally bleaching powder.

The decomposition of the sodium chloride is effected by means of chamber acid (p. 286), for the sake of saving the high cost of concentration, and is carried out in reverberatory furnaces of masonry work. The evolved hydrochloric acid is condensed in large pots of stoneware. The dry sodium sulphate obtained is broken into pieces and mixed with coal and limestone. The reaction between these two substances takes place at a moderate red-heat, and is also carried out in a reverberatory furnace. Since the mass must be stirred in order that the reaction may take place regularly and completely, furnaces have been invented in which this is done by machinery, in order to save the expensive manual labour.

The lixiviation of the fused mass (black ash) is conducted on the principle of counter-currents (p. 455), at 30°-40°, at which temperature the soda is most soluble. On heating the saturated solution, a salt with one combining weight of water of crystallisation, which is less soluble in the heat, is deposited, and this is converted into the anhydrous salt by heating. This is called *soda-ash*, and is generally employed in the large industrial operations. By dissolving this in lukewarm water and allowing it to crystallise in the cold, soda crystals, $Na_2CO_3 + 10H_2O$, are obtained; this is used in operations on a small scale, since it very quickly dissolves.

The soda obtained in this way is rather impure. It contains varying amounts of sodium sulphate, sodium sulphide, and common salt derived from the preparation. Most of the sodium sulphide, certainly, the presence of which is due to incomplete transformation, partly also to the reversal of the reaction with calcium sulphide during the lixiviation, remains in the mother liquor, and is used again in the process.

* If more coal is added than corresponds to the above equations, it acts on the sodium carbonate, along with the water which is present as vapour, and forms sodium hydroxide and carbon monoxide: $Na_2CO_3 + C + H_2O = 2NaOH + 2CO$. In this way caustic soda can be obtained directly; the product, however, is very impure.

* In this process, especial difficulty is given by the residues (*soda-waste*), which consist essentially of calcium sulphide. In the course of time, very different methods have been worked out for obtaining the sulphur from them in some form or other, and at the present day this is successfully carried out in those works where the Le Blanc process is still in use. Since, however, the disappearance of this process is only a question of time, it is not necessary for us to enter into a description of the methods of "sulphur regeneration."

The new method, which on the Continent has practically entirely replaced the older method, depends on the following reactions. Ammonia is absorbed by a solution of common salt, and carbon dioxide then passed in. Sodium bicarbonate, which separates out in the solid state, and ammonium chloride, which remains in solution, are formed. The latter is decomposed with lime into calcium chloride and ammonia, and the ammonia formed is used again in the preparation.

The chemical process, then, amounts to this, that the ions $Na^{\cdot}$, $NH_4^{\cdot}$, Cl', and HCO_3' are brought together in concentrated solution. Under these conditions, there will be deposited, in accordance with principles already laid down (p. 440), that salt which has the smallest solubility; in this case, sodium bicarbonate. It is true that neither ammonia nor carbonic acid alone is dissociated to any great extent into ions, but the two immediately form ions when they come together in solution, since the ammonium bicarbonate is a salt which in solution is dissociated into ions in the same degree as any other neutral salt.

The process would therefore be equally successful if in place of ammonion some other cation were employed, whose bicarbonate is more soluble than sodium bicarbonate. In the case of ammonium, however, there is the special advantage that free ammonia can, on account of its volatility, again be easily recovered from the residual chloride by means of lime.

The chemical reactions, therefore, can be summarised in the following equations:—

$$NaCl + HNH_4CO_3 = NH_4Cl + NaHCO_3$$
$$2NH_4Cl + CaO = CaCl_2 + 2NH_3 + H_2O$$
$$NH_3 + H_2O + CO_2 = HNH_4CO_3.$$

Besides sodium chloride, calcium oxide and carbon dioxide are used up. The latter are obtained from naturally occurring calcium carbonate or limestone, which decomposes into the two constituents on heating. Further, the sodium bicarbonate is placed on the market only in very small amount as such; the greater part is decomposed by heating into normal carbonate and carbonic acid: $2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$.[1]

The soda obtained in this way (Solvay process) is not only cheaper than by the Le Blanc method, but it is also considerably purer.

For special purposes, pure soda is obtained by precipitating the bicarbonate from a concentrated solution of the impure salt by means of carbon dioxide, washing this with cold water and converting it by strongly heating into the normal carbonate.

In analysis, sodium carbonate is employed for several purposes. On the one hand, it is used as a reagent for introducing carbanion, CO_3'', into a given solution; since many carbonates are difficultly soluble in water, the respective cations will be precipitated by this addition. On the other hand, sodium carbonate is used for decomposing various salts at a red-heat, more especially for decomposing silicates and rendering them suitable for analysis. For this purpose, it is mixed with about an equal weight of potassium carbonate. Such a mixture melts much more readily than either of the salts alone. This is another example of the mutual depression of the melting point (*vide* p. 470).

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[1] It is not easy to see why the decomposition of the calcium carbonate and of the ammonium chloride is not united into one operation, for by heating the two ammonium carbonate would be obtained, which could then be dissolved in the solution of common salt. The carbon dioxide from the decomposition of the sodium bicarbonate would then be exactly sufficient to again precipitate sodium bicarbonate from the solution. Presumably technical difficulties have necessitated the indirect process.

Sodium Phosphate.—Of the three sodium salts of orthophosphoric acid, the best known is the disodium salt Na_2HPO_4; this is the salt meant when sodium phosphate is spoken of without further designation. It generally crystallises in large crystals containing $12H_2O$, which readily effloresce; with most of the other sodium salts, however, it shares the property of forming crystals containing different amounts of water, according to the temperature of crystallisation. Thus, more especially, a salt with $7H_2O$ is known which is formed at temperatures above 35°, and is also formed by the efflorescence of the more highly hydrated salt.

At higher temperatures, the salt first loses its water of crystallisation, and then the unreplaced acid hydrogen is given off as water, and there is formed the sodium salt of pyrophosphoric acid: $2Na_2HPO_4 = Na_4P_2O_7 + H_2O$. This is the most convenient method of preparing a pyrophosphate, and from this pyrophosphoric acid (p. 363).

* The above reaction is of great historical interest. The change in the chemical reaction which accompanies the above transformation, led, of a necessity, to the conclusion that the nature of the acid had undergone an essential change by the ignition, and after Clark and Graham had subjected the chemical processes which take place to an exact analytical investigation, and had established the fact that these consist merely in a loss of water, it was possible for Liebig, on the basis of this result, to put forward the *theory of the polybasic acids.* For since at that time (1838) the methods for the determination of the molar weights had not yet been elaborated, all acids were formulated, for the sake of simplicity, as containing only one combining weight of replaceable hydrogen. Liebig showed that the facts could be more consistently and clearly represented by giving up this assumption and writing, where necessary (more especially in those cases where acid salts can be prepared), the formulæ of the acids with two or more combining weights of replaceable hydrogen. This method of formulation received confirmation through the conception of molar weight, which was subsequently developed.

The aqueous solution of disodium phosphate reacts feebly alkaline. The reason of this has already been given (p. 363); the second hydrogen of phosphoric acid is only slightly dissociated, and a certain amount of hydrolysis therefore occurs in the solutions of the corresponding salts.

In the laboratory, the solution of disodium phosphate is employed to introduce phosphanion into reactions. By reason of the nature of the dissociation of phosphoric acid, to which reference has just been made, the solution of the salt contains, to a preponderating extent, the ion HPO_4''. If, as is necessary for most of the precipitations, it is desired to bring the ion PO_4''' into reaction, it is further necessary to add a base, the hydroxyl of which can form water with the hydrogen of the ion HPO_4'', and thereby convert it into PO_4'''. This transformation, it is true, takes place only to a small extent in the solution itself; if, however, the ion PO_4''' is continuously removed from the solution by the deposition of a solid salt, a fresh quantity must always be formed in order to establish chemical equilibrium in the solution, and the object aimed at will be attained. Usually ammonia is the alkali added, because an excess of it does no harm, which is sometimes not the case with an excess of caustic soda or potash.

If to a solution of the ordinary sodium phosphate the quantity of caustic soda required by the equation $Na_2HPO_4 + NaOH = Na_3PO_4 + H_2O$ is added and the solution evaporated, the trisodium phosphate is obtained in hydrated octahedral crystals, which dissolve in water with a strongly alkaline reaction. By addition of phosphoric acid in accordance with $Na_2HPO_4 + H_3PO_4 = 2NaH_2PO_4$, and evaporation, monosodium phosphate is obtained which crystallises in two different forms, each containing $1H_2O$. On being heated this salt passes into the sodium salt of metaphosphoric acid: $NaH_2PO_4 = NaPO_3 + H_2O$.

The sodium salts of pyro- and metaphosphoric acids, which have just been mentioned, are the most important salts of these anions. While the pyrophosphate has only a limited application (in medicine), the metaphosphate is largely used as a reagent in qualitative analysis. It is obtained as a glassy mass by heating monosodium phosphate, and does not crystallise when it is dissolved in water and the solution is evaporated; at a red-heat it has the property of dissolving many metallic oxides, with production of a characteristic colour. In using it, a small quantity is fused to a bead on a loop of platinum wire, and to this is added a small quantity of the substance under investigation. The various heavy metals, more especially, give characteristic colours in the "phosphate bead."

Sodium Silicate behaves quite similarly to potassium silicate, and is employed as soda water-glass (p. 464). Together with other silicates, it occurs both naturally (*e.g.* as albite) and as a manufactured product; thus, for example, ordinary glass is a mixture of sodium and calcium silicates.

Sodium Borate.—Of all the salts of boric acid, a sodium compound is the best known and the most largely used. This salt is called *borax*, and has the composition $Na_2B_4O_7$; it is, therefore, the sodium salt of tetraboric acid, $H_2B_4O_7$, which may be supposed formed from four combining weights of orthoboric acid by the loss of $5H_2O$: $4H_3BO_3 - 5H_2O = H_2B_4O_7$.

Borax is a salt which is not very soluble in water; at lower temperatures it crystallises with $10H_2O$, above 56° with $5H_2O$. The former, or more highly hydrated form, is distinguished as *prismatic* borax from the less hydrated or *octahedral* borax. The relation existing between the two salts is similar to that between Glauber's salt and anhydrous sodium sulphate (p. 485), only the octahedral borax is very easily formed, even in its region of instability below 56°, if nuclei of the prismatic form are excluded.

When heated, borax loses its water, first swelling up to a spongy mass, and then, as the temperature is raised, forming a colourless glass which, on cooling, solidifies in the amorphous condition.

This borax glass has, similarly to sodium metaphosphate, the property of dissolving metallic oxides with production of distinctive colorations, and is therefore used in qualitative analysis for the same purpose as the latter salt. In the case of borax, however, the melting point lies considerably higher, and the colours are also to some extent different, so that the reaction in the borax and those in the phosphate bead must be distinguished. To this solvent power for metallic oxides, the application of borax in *soldering* is also due. Soldering consists in uniting two pieces of metal together by fitting them to one another and filling up the space which is left with an easily fusible metal in the liquid form. In order that such a junction may hold, the liquid metal must wet the surfaces to be united; this is, however, hindered by the layers of oxide with which most of the metals become covered when heated. When the borax melts, it covers the metal, and thus prevents the access of atmospheric oxygen; it also dissolves the oxide which is present, and thus renders the wetting by the liquid metal possible. Borax is used in soldering with difficultly fusible, or *hard solder* (a mixture of copper, zinc, and silver); with easily fusible *soft solder* (tin and lead) there are used zinc chloride, ammonium chloride, resin, or stearic acid, which have a similar action to borax.

Sodium Acetate.—Sodium acetate, $NaC_2O_2H_3 + 3H_2O$, is a salt which is readily soluble in water, and melts at 58° in its water of crystallisation; after the addition of a small amount of water, the fused product can be cooled down without crystallising. With this liquid, which, if "nuclei" are excluded, will keep for years, the experiments on supercooling (p. 116) can be very conveniently performed, since, as a rule, no nuclei of the salt are present in the air, and the apparently spontaneous crystallisation does not readily occur.

In the laboratory, sodium acetate is often employed. It is chiefly used in analytical chemistry for the purpose of preparing solutions which have an acid reaction but contain a very small amount of hydrion. Since several of the precipitates employed for analytical purposes are dissolved by strongly acid liquids, but are sufficiently insoluble in weakly acid ones, an artifice like this is of great importance.

The above object is attained by adding sodium acetate to the solution which contains hydrion, *e.g.* hydrochloric acid (or in which hydrion is formed in the intended reaction). The acetanion thus introduced into the solution combines with the greater portion of the hydrion present to form undissociated acetic acid, since acetic acid is a rather weak acid, and only a small amount of hydrion is left. If more hydrion is formed in the reaction, this undergoes the same transformation, always supposing that there is acetanion still present. The sodium acetate must, therefore, be added in sufficient excess.

The Combining Weight of Sodium has been determined in conjunction with that of silver and chlorine (p. 222) by ascertaining how much silver is necessary for the conversion of a definite amount of sodium chloride into silver chloride, or how much silver chloride can be obtained from a given amount of sodium chloride. In this way it has been found, Na = 23·06.

CHAPTER XXII

RUBIDIUM, CÆSIUM, LITHIUM, AND AMMONIUM

General.—To the two alkali metals, potassium and sodium, which occur very abundantly in nature, there are related three other elements which are found much more sparingly. One of these, *lithium*, has a smaller combining weight than the above mentioned elements, viz., 7·03. The other two, *rubidium* and *cæsium*, have a larger combining weight, viz., 85·4 and 132·9. In their chemical relations, the latter two are quite analogous to potassium, while lithium stands alone in the group, and its chemical analogues are rather to be found in the elements of the next group, that of the alkaline earth metals.

* In view of this circumstance, it may be asked why lithium is not preferably classed along with these other metals. The complete answer to this can be given only after all the assumptions necessary for a comprehensive systematisation of the elements have been discussed. The decisive reason may be here given, viz., that lithium forms a *monovalent* ion, like the alkali metals, whereas the ions formed from the alkaline earth metals are all divalent. The specific heat and other relations are connected with this, and all favour the placing of lithium in the group of the alkali metals. It will also be found that deviations similar to those found in the case of lithium can be frequently and regularly observed.

In this chapter *ammonium* (p. 337) also has been placed, because it forms a monovalent cation $NH^{\cdot}_4$, which is in many respects similar to potassion.

Rubidium and Cæsium.—After the foundations of spectrum analysis had been laid by Bunsen and Kirchhoff in 1860, the former proceeded to apply the new method to several substances. And, indeed, in the mother liquor from the salt wells at Dürkheim, he found new spectral lines which did not belong to any of the elements hitherto known. In a masterly research[1] he separated the corresponding substances and established the fact that two new alkali metals were present, which were especially similar to potassium. From the colour of their most pronounced spectral lines, he called them rubidium (red) and cæsium (blue).

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[1] Bunsen obtained 9 gm. of rubidium chloride and 7 gm. of cæsium chloride from 240 kgm. of mother liquor, corresponding to 44,200 kgm. of mineral water.

The two elements were subsequently often observed, but always in very small amount. Rubidium is found most abundantly in the mother liquors from the Stassfurt potash salts, from which it is separated in the form of its difficultly soluble double salt with aluminium sulphate (alum). Cæsium compounds still remain very rare.

The chemistry of these two elements, so far as investigated, agrees perfectly with that of the potassium compounds. The corresponding salts are generally isomorphous, and exhibit similar solubility relations. More especially do these metals form difficultly soluble salts with hydrochloroplatinic acid, hydrofluosilicic acid, and hydrofluoboric acid; the acid salts of tartaric acid are also difficultly soluble. For this reason there are no methods known by which a tolerably sharp separation of these elements can be effected, and one has to be satisfied with incomplete separations based on slight differences in solubility, which must be frequently repeated before the object is approximately attained.

Thus from the previously concentrated mixture of the three chlorides, by the addition of hydrochloroplatinic acid, Bunsen separated a small precipitate which consisted of the less soluble salts of the two new elements mixed with the more soluble potassium platinochloride. By boiling this precipitate with small quantities of water and adding the portion which passed into solution to the original liquid, he obtained a less and less soluble platinum salt, which finally was almost free from potassium. The separation of rubidium and cæsium was effected by treating the carbonates, or the hydroxides, with alcohol.

Metallic rubidium, which can be obtained by distilling the hydroxide with magnesium, has the density 1·5, melts at 38°, and at room temperature is very soft. It readily volatilises, and ignites spontaneously in moist air and also in dry oxygen. It dissolves in mercury, forming an amalgam, which behaves like potassium amalgam.

In oxygen, rubidium burns to a dark coloured dioxide, RbO_2, which dissolves in water, yielding the hydroxide with formation of hydrogen peroxide and oxygen. The hydroxide is obtained from the sulphate by precipitating the sulphanion with barium hydroxide.

Of the different salts of rubidium, nothing special has to be said.

One peculiarity which is not found in an appreciable degree in the case of potassium, is the property possessed by rubidium and cæsium of forming compounds with the halogens, in which three or five combining weights of the latter to one combining weight of the metal are present; compounds, therefore, in which the metal appears as tri- or pentavalent. Such compounds with bromine or iodine are formed with especial case. They are deposited as difficultly soluble crystalline precipitates of a lustrous yellow to brown colour, on introducing the free halogens into solutions of rubidium bromide or iodide. Through these compounds a similarity is established with the heavy metals thallium and gold (which see) which, for other reasons, have also been ranked along with the alkali metals. These compounds are much more readily formed with cæsium than with rubidium.

Metallic cæsium melts as low as 26°, and is still more readily volatile than rubidium.

Lithium.—From the compounds of the other alkali metals, those of lithium were distinguished by Arfvedson in 1817. Elementary lithium was first prepared in 1855 by Bunsen and Matthiessen, by the electrolysis of the chloride.

Metallic lithium is the lightest of all solid substances; its density is 0·59, so that it floats on petroleum. It is a silver-white, somewhat tenacious metal, which does not melt below 180°, and does not volatilise even at a red-heat. When heated in the air, it does not ignite until considerably over 200°, and it then burns with a white, very bright light, similar to that of magnesium. It decomposes water with evolution of hydrogen and formation of lithium hydroxide; the action is, however, much less violent than with the other alkali metals.

Like the other alkali metals, lithium forms a monovalent, colourless ion $Li^{\cdot}$, which can combine to form salts with all anions. From the ions of the other alkali metals, lithion is distinguished by its power of forming various difficultly soluble salts, which will be mentioned immediately. Lithium is not capable of forming any but monovalent ions.

Lithium Hydroxide is most easily obtained by decomposing lithium sulphate with barium hydroxide. On strongly concentrating the solution, lithium hydroxide, $LiOH$, separates out as a colourless mass, which is readily soluble in water, although not so soluble as caustic potash or soda, but does not deliquesce in air. The solution as, however, essentially the same properties as those of caustic potash nd caustic soda, for lithium hydroxide is dissociated into its ions, $Li^{\cdot}$ nd OH', in almost the same degree as the other alkalis.

The compounds of lithium with chlorine, bromine, and iodine are xceedingly readily soluble, and deliquesce in the air, since their saturated solutions have a smaller vapour pressure than the mean vapour ressure of the water in the air. They dissolve in alcohol and in a nixture of alcohol and ether. Since the chlorides of the other alkali netals are almost insoluble in this mixture, use is made of this proerty for the separation of lithium from these.

Lithium fluoride, however, is very difficultly soluble in water.

Lithium nitrate and *sulphate* are readily soluble in water.

Lithium Carbonate, Li_2CO_3, is difficultly soluble in water, since 00 parts of water dissolve only about one part of the salt. On the ther hand, lithium *bicarbonate* is much more easily soluble, so that nore than 5 parts of the normal carbonate can be dissolved in 100 arts of water if carbon dioxide is passed through the solution. If this solution is heated, carbon dioxide escapes, and the difficultly soluble normal carbonate again separates out. This behaviour can be very well employed in order to prepare lithium compounds pure. It is in marked contrast with that of the other alkali metals, in which case the normal carbonates are much more readily soluble than the bicarbonates. The same behaviour as in the case of lithium is found also in the case of the alkaline earth metals.

Normal Lithium Phosphate, Li_3PO_4, is precipitated from solutions containing lithion, on adding sodium phosphate and ammonia (p. 494). It forms a white, crystalline precipitate, which is very difficultly soluble in water (1 part in 2500 parts of water), and becomes still less soluble in presence of phosphanion. This reaction is used for the detection and precipitation of lithium.

Another and very convenient means of detecting lithium is the red colour which it imparts to a Bunsen flame. Examined with the spectroscope, this coloration is resolved into a red and a yellow line; the latter is situated beside the sodium line, nearer to the red end of the spectrum.

By means of this very sensitive reaction, it can be shown that lithium is a very widely distributed element, although it nowhere occurs in large amount. Thus, tobacco ash generally contains lithium, and when moistened with hydrochloric acid and introduced into the flame of the Bunsen burner, readily shows the red lithium line when examined with a spectroscope.

Metallic lithium combines very readily with nitrogen to form lithium nitride, NLi_3, which is decomposed by water into lithium hydroxide and ammonia. With hydrogen, lithium combines to form a hydride, LiH.

Ammonium.—When discussing ammonia (p. 337), it was stated that that substance unites with water to form an hydroxide which is similar to the hydroxides of the alkali metals in many respects. Its composition is NH_4OH, and its ions are hydroxidion, and the compound cation $NH_4^{\cdot}$, which has been called ammonion, in order to indicate its derivation from ammonia, and its similarity to potassion or sodion.

As a matter of fact, ammonion is found in numerous salts, in which the most various anions are present along with this cation. Not only are these salts of analogous composition to the salts of potassium, the place of potassium being taken by ammonium, but the two series of salts are in almost all cases isomorphous, and exhibit nearly the same solubility relations; the similarities which here exist are, therefore, similar to those that exist, say, between chlorine and bromine, or between potassium and rubidium.

In view of these similarities, the question arises whether besides the ion ammonium there does not exist a non-ion ammonium corresponding to metallic potassium. The answer is only partly affirmative.

If it is attempted to prepare metallic ammonium by the action, say, of metallic potassium on ammonium salts, one does not obtain the compound NH_4, but its decomposition products $2NH_3$ and H_2. The same result is obtained on attempting to decompose a solid or dissolved ammonium salt with the help of the electric current. Only in one special case does one succeed in the latter instance in laying hold of ammonium, at least temporarily, viz., by employing an electrode of metallic mercury. In this way the mercury acquires properties similar to those of a dilute solution of potassium or sodium in that metal, and at the present time there is no great doubt of the existence of an *ammonium amalgam*. Certainly, the amount of ammonia which it contains is always very small, for even in the form of the amalgam, the ammonium undergoes decomposition into ammonia and hydrogen, and its existence is always only a transitory one.

* By reason of this decomposition, gas is evolved throughout the mercury, which thereby acquires a peculiar, spongy character. The ammonium amalgam is very easily obtained by covering a large drop of mercury with a concentrated solution of any ammonium salt and passing an electric current into the mercury, by means of a platinum wire dipping into the solution, in such a way that the mercury acts as a cathode. One accumulator gives a sufficient current. The mercury is at once seen to swell up, and to become converted into a gray, semi-solid mass, which owes its peculiar character to the fact that it is a froth of very small bubbles.

* The same product is obtained still more simply by pouring a concentrated solution of an ammonium salt over sodium amalgam. Metallic sodium then passes into sodion, while ammonion is converted into "metallic" ammonium, or into the products of decomposition of this.

That the ammonium which is formed has to a certain extent the character of a metal, follows from the fact that it is soluble in mercury; for, with the exception of the metals, no other substance has an appreciable solubility in mercury. Besides what has been stated, all that is known concerning the properties of ammonium is that it behaves, electrically, similar to the alkali metals, its position in the "potential series" (*vide infra*) being next to that of the alkali metals.

Ammonion, $NH_4^{\cdot}$, is, as already mentioned, very similar to potassion. Like the latter, it is colourless, and also forms difficultly soluble salts with the precipitants of potassion, tartaric acid and hydrochloroplatinic acid. It can be distinguished from potassion by the readiness with which its hydroxide passes into ammonia, which is volatile.

Ammonium Hydroxide, NH_4OH, is known only in solution, since, on attempting to obtain it in the free state by evaporating off he water, it decomposes into ammonia and water. An aqueous solution of ammonia certainly contains a portion of the dissolved gas as ammonium hydroxide, part of which is in turn dissociated into the ions $NH_4^{\cdot}$ and OH'. What portion of the total ammonia, also, has passed into ions can be determined by measurements of the electrical conductivity. What relation, however, exists between the *undissociated* ammonium hydroxide (NH_4OH) in the solution and its anhydride (NH_3), it has as yet been impossible to determine. It follows, however, from the smell of the solution, that a not inconsiderable portion of the ammonia is present in the uncombined state, since only ammonia, and not ammonium hydroxide, exists in the gaseous state; how great this portion is, however, is unknown.

The electrolytic dissociation of an aqueous solution of ammonia, is very much less than that of an equivalent solution of caustic potash or caustic soda, and, therefore, the strength of ammonia as a base is much less than that of the alkali hydroxides. In a solution containing one mole in ten litres, the concentration of hydroxidion amounts to only 0·016 of that in a solution of caustic potash, and only at a dilution of 100 litres does the fraction amount to as much as 0·042. Consequently, an ammonia solution has a much more feebly basic action than a potash solution, and is employed in those cases where such a feeble action is essential. The concentration of the hydroxidion becomes still less when a large quantity of ammonion is present in the form of an ammonium salt. For since, with a given total concentration of ammonia, the product of ammonion and hydroxidion must have a definite value, the second factor will diminish as the first increases. The relations here are exactly the same as those which have been explained in the case of the hydrion of acetic acid (p. 495).

Connected with this slight degree of dissociation is the fact that an aqueous solution of ammonia can be entirely freed from its ammonia by boiling, in spite of its containing ammonium hydroxide and the ions of this.

This property is used for the detection and determination of ammonium in its salts. These are heated with an excess of a strong base; the hydroxyl of the latter reacts with the ammonium with formation of water and ammonia, and the latter is driven off by the heating. If it is only a case of detecting the presence of ammonia, it is sufficient to hold a piece of wet, red litmus paper over the heated liquid; ammonia turns the litmus paper blue. For the same purpose a glass rod moistened with strong hydrochloric acid can be used (p. 338). If it is desired to determine the amount of ammonia, the liquid is distilled into a measured amount of acid of known titre; after the distillation, the amount of acid which has not been neutralised by the ammonia is determined by titration with a solution of barium hydroxide (p. 187).

Ammonium Chloride.—Of the salts of ammonium, ammonium chloride or sal ammoniac, NH_4Cl, is the best known. It is a white salt which is readily soluble in water; it crystallises in the regular system, but has a marked tendency to imitate the forms of other systems

At about 450° it volatilises, without melting, in the form of colourless vapours. These, however, do not consist of ammonium chloride, but are a mixture of hydrogen chloride and ammonia. This is seen from their density, which does not yield the value 53·5, the molar weight of ammonium chloride, but only half this value. It can be easily shown by diffusion (pp. 92 and 287) that the vapour is indeed a mixture; the lighter ammonia passes much more rapidly through a porous partition than the heavier hydrogen chloride, and for this reason, the portion which has passed through reacts alkaline, the portion which remains, acid.

* This dissociation occurs only when the ammonium chloride contains a trace of moisture. If the salt is carefully dried, the decomposition takes place so slowly that its density in the undissociated state can be determined. That we are here dealing with a catalytic acceleration by means of the water vapour, follows from the fact that the opposite reaction, the combination of hydrogen chloride and ammonia to ammonium chloride, also occurs rapidly only in presence of water vapour. If the two gases are very carefully dried, they can be mixed without any fumes of ammonium chloride being produced. This is a good example of the general law that a catalyser which accelerates a certain reaction, must also accelerate the reverse reaction.

The aqueous solution of ammonium chloride exhibits a feebly acid reaction which is due to the slight hydrolysis of the salt. A small amount of ammonion reacts with hydroxidion from the water to form ammonia and water, and the corresponding amount of hydrion remains over and causes the acid reaction. As ammonium chloride is a salt of the strong acid, hydrochloric acid, hydrolysis is small, but will, of course, become all the greater the weaker the acid of the ammonium salt is. If the solution is heated to boiling, a portion of the ammonia produced distils off, and the acid reaction increases.

Ammonium chloride is used for many purposes, both in the laboratory and in the arts. Its use in soldering depends on the splitting off of hydrogen chloride on heating, whereby the coating of oxide on the metals to be soldered is removed. Its further applications for obtaining those chlorides which are readily decomposed by water with loss of hydrogen chloride, and as "exciting salt" in the Leclanché galvanic cell, also depend on the splitting off of hydrogen chloride.

Ammonium Bromide and Ammonium Iodide are employed in photography. The former is a white salt similar to ammonium chloride; the latter is also white when pure, but it is difficult to preserve it colourless, as it speedily becomes brown. This is due to the fact that it is slightly dissociated hydrolytically when it becomes moist in the air, *i.e.* when some solution is formed. The hydriodic acid, however, which is split off is immediately oxidised by the atmospheric oxygen (p. 234), free iodine is formed, and the same series of reactions occurs over again. The salt can be preserved by excluding air and moisture.

Ammonium Nitrate.—This salt has already been mentioned on a former occasion (p. 341), since on account of its decomposition into nitrous oxide and water on heating, it is used for the preparation of that gas. It is obtained as a very soluble salt by neutralising nitric acid with ammonia or ammonium carbonate, and evaporating. When thrown on red hot charcoal, it decomposes with production of flame; alone, or mixed with charcoal, it can be made to explode, and it is therefore used in the preparation of explosives. These are ignited with difficulty, and can therefore be used without danger. Since the substance is converted completely into gases and vapours, the explosive effect is an advantageous one, especially as the nitrous oxide formed gives out a considerable amount of heat on decomposing (p. 331).

Ammonium Nitrite, NH_4NO_2, is of interest on account of its ready decomposability into water and nitrogen (p. 341); in the free state it is known only as a deliquescent and decomposable crystalline mass.

Ammonium Sulphate, $(NH_4)_2SO_4$, is isomorphous with potassium sulphate, but is much more readily soluble in water than the latter. Similarly to potassium sulphate, it forms various double salts, more especially with the divalent sulphates of the magnesium group and with the trivalent sulphates of the aluminium family. The solution is somewhat more strongly dissociated hydrolytically than that of ammonium chloride. If the solid salt is heated, it loses ammonia and passes into the acid ammonium sulphate, NH_4HSO_4; this is a reaction which is peculiar to the normal ammonium salts of all polybasic acids

Ammonium Phosphates.—Of the three possible ammonium phosphates, only the first two are known, the mono- and the di-ammonium phosphate, since the normal salt decomposes so readily into ammonia and diammonium phosphate that it does not keep. The salts are of no special importance.

A salt which is better known is sodium ammonium phosphate, $NaNH_4HPO_4 + 4H_2O$, or microcosmic salt. It is used instead of sodium metaphosphate for blowpipe experiments, since it passes into the latter salt on heating. The decomposition takes place according to the equation $NaNH_4HPO_4 = NaPO_3 + H_2O + NH_3$. Since this decomposition is accompanied by a considerable swelling up of the salt, it is more convenient not, as is usually done, to first prepare the "phosphate bead" on the platinum wire immediately before the experiment, but to directly employ sodium metaphosphate. The name *microcosmic salt* is due to the fact that the compound is formed in the evaporation of human urine (decomposed by putrefaction). This liquid excretion of the useless constituents of the organism was regarded by the alchemists as an extract of the human microcosm.

Ammonium Carbonate.—Normal ammonium carbonate is very unstable, since it undergoes with great readiness the general decomposition of the ammonium salts of polybasic acids. On the other hand.

the acid salt NH_4HCO_3 is very stable, and scarcely smells of ammonia. It crystallises from solutions of ammonia which have been saturated with carbon dioxide. The two salts combine with one another to form a double salt, the so-called ammonium sesquicarbonate $(NH_4)_2CO_3 + 2NH_4HCO_3$, which forms the chief constituent of commercial ammonium carbonate. The latter usually also contains ammonium carbamate or the ammonium salt of carbamic acid (p. 394), which is produced from the normal carbonate by loss of water: $(NH_4)_2CO_3 = NH_4OCONH_2 + H_2O$.

Ammonium Sulphide.—The two compounds which sulphuretted hydrogen can form with ammonium are largely employed in the laboratory. They are prepared by passing sulphuretted hydrogen gas through a strong solution of ammonia. With excess of sulphuretted hydrogen, ammonium hydrosulphide, NH_4HS, is formed in the solution; if to this is added as much ammonia as was originally taken, a solution of ammonium sulphide, $(NH_4)_2S$, is obtained. The latter solution does not contain solely ammonium sulphide and its ions, any more than the corresponding compound is alone contained in the solution of the alkali sulphides (p. 460); on the contrary, hydrolysis proceeds further in this case than in that of the latter, for we are here dealing with the salt of a weak base with a weak acid. For those reactions, however, in which sulphidion is consumed, the actual condition of the solution is of comparatively little importance, since the sulphidion which is used up in the reaction can be produced afresh in proportion as it passes out of the solution.

Both the above salts can be obtained in the solid state by mixing sulphuretted hydrogen and ammonia gas in the necessary proportions: $NH_3 + H_2S = NH_4HS$ and $2NH_3 + H_2S = (NH_4)_2S$. In this way, crystalline masses are obtained the vapour density of which shows that, on vaporisation, they again decompose into their components. The sulphide is exceedingly readily volatile, the hydrosulphide less so.

* In the case of ammonium hydrosulphide, thorough investigations have been made concerning the equilibrium between the solid salt and its vapour. If we denote the concentrations of the ammonia and of the sulphuretted hydrogen by a and b respectively, and by c the concentration of ammonium hydrosulphide in the vapour (this is, indeed, very small but not zero), then, in accordance with the general equation of equilibrium (p. 326), we have the relation $ab/c = k$. The concentration of the undissociated ammonium hydrosulphide is dependent solely on the temperature, since, according to Dalton's law, the vapour pressure of a given substance remains the same whether other substances are present in the gas space or not. For each temperature, therefore, the product ab must also be constant. It is a case of an equilibrium, therefore, which is perfectly similar to that between a solid salt and its partially ionised solution (p. 440). As a matter of fact, also, the following peculiarities were found:—

(*a*) If there is no excess of one of the components in the gas space

($a = b$), a definite dissociation pressure is established which is dependent only on the temperature, and not on the relative amounts of solid substance and vapour.

This follows from the equation, for if $a = b$, the value of c can depend only on the temperature; for the equation then assumes the form $a^2 = kc$, and k as well as a depends only on the temperature.

(b) Less of the solid substance evaporates into a space in which ammonia or sulphuretted hydrogen is already present; the effect of equal excesses of the two gases is equal. This also corresponds to the equation, for the expression ab/c is symmetrical in respect of a and b.

* The equilibrium of ammonium sulphide would necessarily be represented by an equation of the form $a^2b/c = k$, because two moles of ammonia react with one mole of sulphuretted hydrogen. The decomposition of ammonium sulphide, however, does not take place in such a way that the two gaseous components are formed, but in such a way that ammonium hydrosulphide is produced along with free ammonia. The conditions of equilibrium become thereby complicated, and will not be discussed here.

The aqueous solution of ammonium sulphide rapidly becomes coloured yellow in the air, because the sulphuretted hydrogen which is split off by hydrolysis is oxidised by the atmospheric oxygen (*vide* p. 275); the sulphur which is formed dissolves in the excess of ammonium sulphide to form polysulphides, corresponding to the alkali polysulphides (p. 461). A tetra- and a heptasulphide of ammonium, $(NH_4)_2S_4$ and $(NH_4)_2S_7$, have been prepared in the solid state.

In the laboratory, ammonium sulphide is used for the precipitation of those metallic sulphides which are dissolved by free acids. The theory of these precipitations has already been given (p. 274). Potassium or sodium sulphide have the same action, but ammonium sulphide is preferred, because an excess of it can be more easily removed from the solution.

Yellow ammonium sulphide is used for dissolving those metallic sulphides whose higher sulphur compounds can pass into thio-acids and form soluble ammonium salts. Tin sulphide is an example of this. Further information on this point will be given under the respective metals.

Besides being used for obtaining sulphur compounds, ammonium sulphide is also used as a reducing agent, especially in organic chemistry. The action depends on the corresponding properties of sulphuretted hydrogen (p. 275); ammonium sulphide has the advantage that the reagent can be used in a much more concentrated form than the slightly soluble sulphuretted hydrogen. Hydrogen is used up in the reaction, the sulphur is precipitated, and ammonia is liberated. Fresh sulphuretted hydrogen can then be passed into the solution, if it is necessary to continue the reduction.

CHAPTER XXIII

CALCIUM

General Remarks on the Alkaline Earth Metals.—The metals of this new group are distinguished from the alkali metals, essentially by their power of exclusively forming divalent ions. This is seen from the fact that, *e.g.*, the amount of calcion which can combine with a given amount of chloridion, does not depress the freezing point of the aqueous solution by the same amount as the chloridion, but only by half as much. One molar weight of calcion, therefore, combines not with one but with two molar weights of chloridion, and for this reason it must be regarded as divalent.

* Since the different ions cannot be handled separately, the above result was obtained indirectly. If very dilute solutions of potassium chloride and of calcium chloride are prepared, in which the concentrations of the chloridion are the same, and the freezing points are determined, the depressions of the latter are not equal but are in the ratio of 4 : 3. Since, in the case of potassium chloride, an equal share of the depression is due to each of the ions,[1] the share of the chloridion in the solution of calcium chloride must also be put equal to two, and the calcion has only the effect one, *i.e.* acts half as strongly as the potassion. From this the above conclusion follows.

Other differences, although not so decisive, are found in the solubility relations of the salts. Thus, for example, the normal carbonates and phosphates of the alkaline earth metals are very difficultly soluble in water, indeed it is only the alkali metals that can form readily soluble salts with the ions carbanion and phosphanion (and with a series of similar ions). It has, however, just been specially mentioned that in this respect lithium forms a transition.

The metals of this group are less sensitive to free oxygen and to oxygen compounds than the alkali metals; they are also much less readily fusible and volatile than the latter. Here also the same gradation is observed, for the tendency to combination with oxygen and to ion formation is least in the case of the elements with small combining weight, and distinctly increases as the combining weight rises. The hydroxides of the alkaline earth metals are slightly soluble in water, but in their solutions they are dissociated into their ions just as the hydroxides of the alkali metals.

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[1] This is seen from the fact that one mole (= 74·6 gm.) of potassium chloride gives a depression of the freezing point which is twice as great as that given by one mole of an undissociated substance.

Calcium.—The compounds of calcium have an exceedingly wide distribution in the earth's crust, and form one of the most abundant constituents of the latter. It is the carbonate chiefly that occurs in nature; in the silicates of the earth's crust, also, calcium is seldom absent. The element also takes part in the most varied way in the building up of the organisms.

Metallic calcium was comparatively late in being prepared in the pure condition. Davy and Berzelius, at the beginning of the nineteenth century, attempted to obtain it from the electrolytically prepared amalgam by distilling off the mercury, but they did not obtain a sufficiently pure material to allow of its properties being ascertained. Nor have the later experiments carried out by different investigators yielded a pure metal, as can be judged from the contradictory statements regarding its properties. The most recent investigations, in which calcium iodide was decomposed with sodium whereby, after removal of the excess of sodium, crystallised calcium is obtained, show that this element is a white (not, as previously stated, a yellow) metal which can be re-melted in a vacuum at 760° and can then be cut; it is, however, not so soft as potassium. It is not affected by oxygen, chlorine, bromine, or iodine at the ordinary temperature, but combines with these only on being heated. When heated in the air, it burns, forming a compound both with the oxygen and the nitrogen. It is only slowly attacked by water, but quickly by dilute acids.

Calcion.—Calcium forms only one kind of ion, viz. divalent calcion. $Ca^{\cdot\cdot}$. The heat of formation of this from the metal is 458 *kj.* In using this number for the calculation of the heats of formation of dissolved calcium salts, it has to be noticed that the heats of formation of monovalent anions must be doubled in the calculation.

Solutions which contain calcion have no immediately conspicuous properties; thus, they are colourless when no other substance possessing a colour is present. Since there are a considerable number of difficultly soluble calcium salts, there are a correspondingly large number of substances by means of which precipitates can be produced in solutions containing calcion. For our purpose, two of these are especially important, viz., the anion of carbonic acid, CO_3'', and that of oxalic acid, C_2O_4''. The latter, more especially, is a specific reagent for calcion: for it forms with it the very difficultly soluble calcium oxalate, which is deposited as a fine, white precipitate when the two kinds of ions come together in solution.

No "complex" ions are known in which calcium forms a part; wherever, therefore, calcium is present in aqueous solution, calcion is also present.

Calcium Hydroxide and Calcium Oxide.—Its ion being divalent, calcium unites with two combining weights of hydroxyl to form calcium hydroxide, $Ca(OH)_2$. This compound, whose common name is *lime* or *slaked lime*, is a white powder which is only very slightly soluble in water. One litre of water dissolves about 2 gm. of lime. The solubility decreases with rising temperature, so that *lime-water* (as the solution of calcium hydroxide is usually called) which has been saturated at the room temperature becomes distinctly turbid when heated to boiling. This behaviour is connected with the fact that calcium hydroxide dissolves in water with evolution of heat.

The aqueous solution exhibits the character of hydroxidion in its alkaline reaction towards vegetable colours, such as litmus, etc. The determination of the electrical conductivity shows that the electrolytic dissociation in solution is almost complete; in this sense, therefore, calcium hydroxide is a strong base. Since, however, its slight solubility allows of only a correspondingly small concentration of hydroxidion being attained, lime-water is used in medicine as well as in the laboratory, in cases where it is desired to produce only slightly basic effects.

In the air, lime-water becomes covered with a thin film consisting of calcium carbonate, which is very difficultly soluble in water. If a gas which contains even only a small amount of carbon dioxide is passed through clear lime-water, this at once becomes turbid owing to the separation of carbonate. For this reason, lime-water is greatly used as a reagent for carbon dioxide and carbonates.

Lime-water is prepared by shaking up lime with water and allowing the mixture to stand in a closed bottle until the excess of solid has sunk to the bottom; the clear liquid which is left is used directly. Filtration is a useless labour, since in contact with the air so much carbon dioxide is taken up that the liquid becomes turbid, and an indefinite amount of the dissolved lime is lost.

On account of its small solubility, lime is frequently employed as a mechanical suspension in water. If the mixture so obtained is a thin liquid, it is called *milk of lime*; if not, it is called *lime paste*. Since of all the strong bases lime is by far the cheapest, it is employed in chemical manufactures in all cases where a strong base is necessary, and where its properties, or the properties of the compounds formed, allow of it.

Calcium hydroxide is obtained exclusively from *calcium oxide*, which, in turn, is obtained by heating calcium carbonate. For since calcium hydroxide contains two combining weights of hydrogen, it gives rise to the formation of an anhydride with comparative ease, just as many dibasic oxyacids give an anhydride more easily than monobasic acids. At the temperature of a red heat, calcium hydroxide loses water and yields calcium monoxide or calcium oxide : $Ca(OH)_2 - H_2O = CaO$; and, conversely, calcium hydroxide is readily obtained from the latter by absorption of water.

The method of obtaining calcium oxide (*quick-lime*) depends, as has been mentioned, on the decomposition of calcium carbonate when heated. This salt decomposes into calcium oxide and carbon dioxide: $CaCO_3 = CaO + CO_2$. The very interesting secondary conditions connected with this decomposition will be given later.

The quicklime obtained in the above manner forms irregular lumps, which exhibit on a smaller scale the form of the limestone employed, and is generally coloured brown or gray. The colour, however, is due only to impurities; if pure calcium carbonate, *e.g.* white marble, is used, the quicklime is also white.

When exposed to the air, quicklime takes up water and carbonic acid and crumbles to a white powder, which is a mixture of calcium hydroxide and calcium carbonate; in this process the substance expands very considerably. If quicklime and water are brought into contact with one another in the cold, no action, apparently, takes place; gradually, however, the mass becomes warm, and then the two substances rapidly combine with considerable evolution of heat to form hydroxide. This process is called the *slaking* of lime. If not too large a quantity of water has been taken, the heat evolved is sufficient to drive off the excess of water, and a snow-white, dry powder of calcium hydroxide, considerably increased in bulk, is obtained. If, however, the product is intended to be used directly, more water is taken, and a thick, white paste is obtained which contains the slaked lime in a state of very fine division, specially suitable for its further use.

Quicklime is very resistant to heat, as it does not melt below about 3000°. It is used, therefore, in the manufacture of heat-resisting apparatus, especially for the fusion of platinum in the oxyhydrogen blowpipe. If heated to about 2000°, quicklime emits a very strong, white light. The "lime light" produced by the oxyhydrogen blowpipe, which was formerly very important, has greatly lost in importance through the ease with which a very powerful electric light can be obtained.

Soda Lime is a material very largely used in the laboratory for the purpose of absorbing carbon dioxide in analysis, and for other purposes. It is not a chemical compound, but a mechanical mixture which is prepared by slaking quicklime with a solution of caustic soda and drying the paste produced. Soda lime acts best when used in not too fine grains; it can be obtained in this form commercially. In the absorption of carbon dioxide, water is liberated. The soda lime is usually placed in U-tubes, and at the end at which the gases issue, a short layer of calcium chloride is placed in order to retain the escaping water.

Calcium Carbonate.—It has already been stated that calcium carbonate is the most widely distributed, and therefore also the most important salt of this metal. In various forms as limestone, chalk, marble, etc., it forms large rocky masses, which always go on increasing by reason of the processes taking place on the earth's surface.

The naturally occurring calcium carbonate is found in two different crystalline forms, which in their pure formations are known as calc-spar and aragonite. Calc-spar has the density 2·71, and crystallises in the trigonal system, generally in rhombohedra; aragonite has the density 2·94, and crystallises in rhombic prisms.

* When at the commencement of the nineteenth century it was established by the methods of quantitative analysis, which had just then been elaborated, that these two well-known minerals have a perfectly identical composition, one came into conflict with the then accepted principle that different form and different composition always correspond to one another. An apparent explanation was yielded by the discovery in aragonite of strontium, whose carbonate crystallises in the same forms as aragonite; the explanation was, however, only a passing one, for specimens of aragonite were soon found in which no trace of strontium could be detected. Not until it was discovered in a number of other substances, especially in the case of sulphur (p. 253), that these could have different forms although possessing the same composition, was the conception of *polymorphism* (p. 238) put forward by Mitscherlich, and the explanation of the regularity which is here present given.

Calc-spar and aragonite are monotropic (p. 255); and calc-spar is the stable, aragonite the unstable form. This follows from the fact that aragonite, on being heated to about 300°, changes spontaneously into calc-spar, whereby it swells up and crumbles to a sandy powder possessing the density of calc-spar. Further, that the above is the case is shown by the fact that aragonite is more readily soluble than calc-spar.

* The determination of such small solubilities as those of the two forms of calcium carbonate, is accomplished by measurement of the electrical conductivity. The conductivity of as pure water as possible increases by a measurable amount when it is brought into contact with the above substance, and this increase is about 15 per cent greater in the case of aragonite than in the case of calc-spar.

Besides these two crystalline forms of calcium carbonate, there is also an amorphous form which is always the first to appear when calcium carbonate is precipitated from a solution. This form is the least stable, and therefore, also, the most soluble; it is so soluble that it has an alkaline reaction to litmus. At a higher temperature it readily passes into aragonite, which is converted only exceedingly slowly into calc-spar; at low temperatures, it is converted directly into calc-spar. When, therefore, calcium carbonate has been obtained by precipitation, either in analysis or in its preparation, it must be allowed to stand some time, preferably in the heat, in order that the amorphous soluble salt may be converted into the difficultly soluble, crystalline form.

The purest naturally occurring form of calc-spar, which is found chiefly in Iceland, is called *Iceland spar*. By reason of the peculiar way of refracting light possessed by the monoaxial crystals, the large and perfectly transparent crystals in which this form occurs show objects double, owing to the light being resolved into two bundles of polarised rays. On account of this property, these crystals are much used for optical instruments; Iceland spar is used more especially for the construction of prisms for polarising light.

Marble and limestone are more finely crystalline and less pure forms of calc-spar; both consist of small, intergrown crystals of calc-spar. Finally, chalk consists of small, roundish grains; that these are of calc-spar is not quite certain.

* That the naturally occurring aragonite, which in some cases is undoubtedly thousands of years old, has not yet been entirely converted into calc-spar, is to be accounted for by the exceeding slowness of the transformation. In many places where accelerating influences have been at work, pseudomorphs of calc-spar on aragonite, *i.e.* masses having the outward form of aragonite but whose substance has become converted into calc-spar, can be found.

When calcium carbonate is heated, it decomposes into calcium oxide and carbon dioxide. This chemical process, "lime burning," is one of the oldest chemical operations, for the lime which is formed has been used as mortar for thousands of years. Decomposition takes place in accordance with the law that for each temperature there is a definite concentration, or a definite pressure, of the carbon dioxide, at which equilibrium exists. If this pressure is increased, carbon dioxide is taken up by the lime present; if it is diminished, another portion of the carbonate decomposes, until the equilibrium pressure has been again established. In the following table a number of different temperatures with the corresponding pressures are given:—

Temperature.	Pressure in cm. mercury.
547°	2·7
610°	4·6
625°	5·6
740°	25·5
745°	28·9
810°	67·8
812°	75·3
865°	133·3

The equilibrium or dissociation pressure of calcium carbonate follows the same law as the vapour pressure of a volatile liquid; in particular, it is independent of the proportions in which the two solid substances, calcium carbonate and lime, are present; it is also independent of the relative amounts of the solid and gaseous phases.

* This follows as a necessary consequence from the phase law. There are two components, lime and carbon dioxide, from which all the phases present can be compounded. Since there are three phases present, viz., carbon dioxide, lime, and calcium carbonate, there is still one degree of freedom, *i.e.* to each temperature there corresponds a perfectly definite pressure, and the amounts of the phases have no influence.

As an examination of the table shows, the "burning" of lime by mere heating cannot be carried out under a temperature of 812°, since it is not till this temperature that the pressure of the carbon dioxide reaches one atmosphere and the escape of gas is assured. Since, however, this equilibrium depends not on the absolute pressure but only on the partial pressure of the carbon dioxide, the decomposition can be carried out at a much lower temperature by keeping the partial pressure of the carbon dioxide sufficiently low. This can be done by allowing another gas, most simply air, to stream over the heated carbonate; at each moment, then, there escapes (at most) so much carbon dioxide that the partial pressure corresponding to the particular temperature is established.

The great similarity which this phenomenon bears to that of the boiling and evaporation of volatile liquids, is easily seen. The temperature of 812° is, so to say, the boiling point of calcium carbonate.

The use of lime for mortar, which has already been mentioned several times, depends on the converse change into calcium carbonate. Mortar is a mixture of lime, sand, and water; in using it, the stones which have to be cemented together are moistened with water, a layer of mortar is introduced between them, and the whole is left to the influence of the atmosphere. By means of the carbon dioxide which he latter contains, the calcium hydroxide is slowly converted into carbonate, water being thereby set free: $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$. The crystals of carbonate, which are slowly formed, unite with one nother and pass partly into the pores of the stones, the solubility of he lime enabling a certain, although small, amount of it to get in there. In this way the well-known firm cementing together is gradually produced, and becomes firmer as time goes on, since even in very old mortar there is usually a certain amount of hydroxide present.

The fact that water is set free in the hardening of mortar under the ction of carbon dioxide is the explanation of the phenomenon that ewly built plaster walls, even when they appear dry, again become wet when the rooms are inhabited, for more water is set free by the ncreased amount of carbon dioxide derived from the expired breath of he inhabitants.[1] The common method of drying newly built houses y means of open coal fires depends, therefore, for its action, not only on the heat produced, but at least as much on the carbon dioxid formed ; for this reason it is important that this latter be not agai removed by means of a strong draught of air, but that, on the contrary, the change of air should be limited so as to allow of a lon period of action.

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[1] An adult man expires daily about 1 kgm. of carbon dioxide.

Calcium Bicarbonate.—The solubility of calcium carbonate (i both its forms) increases considerably when carbon dioxide is presen in the water. This is due to the formation of calcium bicarbonate $Ca(HCO_3)_2$. This salt is not known in the solid state, but th increase in the solubility, just mentioned, is without doubt to b accounted for by the formation of the monovalent hydrocarbanio HCO_3', because every case of increase of the solubility of a sal depends on the decrease of its original ions or on the formation of new ions in the solution (p. 439).

In answer to the question why calcium bicarbonate cannot, lik potassium or sodium bicarbonate, be prepared in the solid state, i must be remarked that the dissociation pressure of carbon dioxid from the solid salt has probably a considerable value even at th ordinary temperature. For it would be just as little possible t prepare the bicarbonate of the alkali metals from their solutions if on were compelled to work at 100°, without employing a higher pressure By increasing the pressure of the carbon dioxide, and keeping the temperature as low as possible, there is first of all an increase in th amount of bicarbonate formed in the solution ; when in this way th point of saturation has been reached and exceeded, the bicarbonate o the metal present must separate out in the solid state.

To the ready decomposability of the bicarbonate is due the migration of calcium in nature. In localities where carbon dioxide is forme and absorbed by water, it at once proceeds to dissolve the calciu which is everywhere present, and thus spring water, and, to a smalle extent, also river water, carries off corresponding amounts of calciu in solution. This is deposited as normal carbonate when by an means (evaporation in the air, or consumption by organisms) carbo dioxide escapes from the water. In the case of waters rich in carbonic acid, *e.g.* those of Carlsbad, this process is very distinctly seen for the carbon dioxide which is dissolved under excess of pressure rapidly escapes, and causes the water to immediately deposit large quantities of calcium carbonate (thermal tuff).

The large amounts of calcium which are in this way introduced into the ocean, are to a very considerable extent separated from it by the organisms which live there, and which use the calcium carbonate to build up their shells and framework. Another portion is deposited in consequence of the consumption of the carbon dioxide by the marine vegetation. In the course of time all these masses are deposited on the sea floor, and there give rise to the very extensive layers of calcium carbonate which, in the form of limestone, constitute such a considerable portion of the earth's crust. It has already, on a former occasion (p. 423), been stated that by the above process more and more carbon is gradually withdrawn from the organisms, because the chemical reactions by means of which the carbon dioxide is again withdrawn from the limestone are neither very numerous nor very productive.

* The solvent action of water containing carbonic acid is the cause that practically no fossils, *i.e.* remains of former organisms, are found in sandstone formations. For these remains consist chiefly of the skeletal portions formed of calcium carbonate. Where the embedding rocks are formed by calcium carbonate, the infiltrating water is saturated with this salt, and does not therefore attack these remains. In sandstone, however, which consists of quartz, the water contains an excess of carbon dioxide, and therefore exerts a solvent action on any calcium carbonate present. If the dissolution does not occur till after the object has become surrounded by a hard crust, although the object itself is dissolved, there remains a hollow mould which subsequently becomes filled with other material, and in this way many forms have been preserved.

The dissolved salts of the alkaline earth metals are the cause of the "hardness" of water, a property which finds expression in the fact that such water cannot be used for washing. This is due to the soap reacting with those soluble salts to form insoluble compounds which are not suitable for washing purposes. Since the carbon dioxide contained in the water can be removed by boiling, and the corresponding amount of calcium carbonate be thereby precipitated, the hardness of a water containing bicarbonate is thus diminished. A distinction is therefore drawn between temporary and permanent hardness; the former is caused by the calcium which is dissolved as bicarbonate and disappears on boiling, the latter is due to other calcium (and magnesium) salts, and continues to exist.

The calcium carbonate which is precipitated in this way also constitutes "boiler incrustation," *i.e.* the precipitate which is formed in vessels in which water is heated to boiling. If the water is not only heated to boiling but is completely evaporated, as in steam boilers, the incrustation of course consists of all the solid substances which were dissolved in the water and are deposited on its removal. Such boiler incrustation generally consists chiefly of calcium sulphate.

Calcium Chloride.—Calcium chloride is a colourless salt very readily soluble in water; it is known in the anhydrous condition, and in forms containing from 1 to 6 moles of water of crystallisation. There are at least five different hydrates of this salt; with rising temperature, some of these exhibit consecutive regions of stability, whereas other hydrates are unstable, like sodium sulphate with $7H_2O$ (p. 484). The best known is the hexahydrate, $CaCl_2 + 6H_2O$, which separates out from concentrated solutions at a low temperature and forms large, transparent, and deliquescent crystals. On warming the salt, it melts completely in its water of crystallisation, and if the heating is continued, a spongy mass of monohydrate or of anhydrous salt, according to the temperature employed, is left behind and fuses at a bright red heat. On fusing, the red-hot salt readily gives off hydrochloric acid, if water vapour is allowed to act on it, $CaCl_2 + H_2O = CaO + 2HCl$, and the salt, after fusion, then reacts alkaline. This decomposition can be avoided to some extent by conducting the fusion in an atmosphere of hydrochloric acid, which is most easily accomplished by adding ammonium chloride during the evaporation; this volatilises on heating to redness, and thereby decomposes into ammonia and hydrochloric acid (p. 503).

Calcium chloride is formed as a by-product in many chemical operations (cf. p. 492), and has scarcely any industrial application. In the laboratory it is used as a convenient desiccating agent for gases; for this purpose it is better to use not the fused salt but the dried spongy mass, which has a quicker action. Like all desiccating agents, calcium chloride does not remove the water vapour entirely, but only to such a degree that the vapour pressure is equal to the vapour pressure of the hydrates present (p. 485). For most purposes this is certainly small enough; still, the aqueous vapour pressure from concentrated sulphuric acid, for example, is very much smaller, and this is therefore a much more perfect desiccating agent.

* Calcium chloride must not be used for drying ammonia, since it combines with this to form a white mass having the composition $CaCl_2 + 4NH_3$. Even at the ordinary temperature, this substance gives off ammonia under a small pressure, and to each temperature there corresponds a definite pressure of ammonia. It is a case of chemical equilibrium of quite the same character as that between calcium carbonate, lime, and carbon dioxide; in this case the two solid phases are calcium chloride and its ammonia compound, and the gaseous phase is ammonia.

Another application of calcium chloride, which also depends on its great solubility, is to produce powerful freezing mixtures. A saturated solution of calcium chloride does not freeze till − 37°, and therefore the temperature of a mixture of crystallised calcium chloride and ice falls to that point. It is necessary to use crystallised, and not fused salt; the latter is much less efficient, because it dissolves in water with considerable rise of temperature, while the crystallised salt with $6H_2O$ dissolves with considerable lowering of temperature.

Calcium Hypochlorite and Bleaching Powder.—To render the chlorine for bleaching purposes suitable for transport, it is absorbed by lime. In this way a white powder smelling of chlorine is obtained; it contains about 30 per cent of chlorine, and it gives this up in almost undiminished amount when the lime is converted by an acid into the corresponding salt. This product is called *bleaching* *powder.* It is prepared and used in very large amounts. Its use also is not confined to bleaching, but it is also employed for disinfecting, for oxidising, and for many other purposes in preparative chemistry. We have found it previously to be a convenient means of preparing chlorine (p. 166).

Bleaching powder can be regarded as a mixture or as a compound of calcium hypochlorite and calcium chloride, formed in accordance with the equation $2CaO + 2Cl_2 = CaCl_2 + Ca(OCl)_2$, or $CaO + Cl_2 = Ca\begin{matrix}Cl\\OCl\end{matrix}$, and having the composition here represented. Much discussion has taken place as to which of the two formulæ is to be preferred, but no decision has been arrived at. This is connected with the fact that it would be difficult to state in what essential point two compounds having the composition represented by the two formulæ would differ.[1] In aqueous solution, at all events, no difference between the two formulæ exists, since in it essentially the separate ions $Ca^{\cdot\cdot}$, Cl', and OCl' are present.

By acids of all kinds, even by the weak carbonic acid, as much chlorine is liberated from bleaching powder as was used in its preparation. This is most easily seen by writing the ionic equations. On bringing together two combining weights of hydrion with the above mentioned anions of bleaching powder, the reaction occurs: $Cl' + OCl' + 2H^{\cdot} = Cl_2 + H_2O$. Since in this reaction hydrogen ions are used up, actual ions are not required for the process, but potential (p. 245) ones are sufficient.

The oxidising actions of bleaching powder depend on the presence of hypochlorosion, OCl', which can pass into chloridion with loss of oxygen: $OCl' = Cl' + O$.

* The bleaching powder which is prepared commercially, is not a pure compound, and it is therefore necessary to determine the amount of its available chlorine. The amount also changes with time. This depends, on the one hand, on the fact that the bleaching powder loses oxygen, the hypochlorite thereby passing into chloride, $Ca(OCl)_2 = CaCl_2 + O_2$, and partly on a transformation of the hypochlorite into chlorate, corresponding to the reaction described on p. 211. Although the chlorates in presence of chlorides also evolve chlorine under the action of acids, this reaction is much slower and requires more concentrated solutions than is the case with the hypochlorite, so that it does not occur to an appreciable extent under the conditions under which bleaching powder is usually employed. Finally, in the case of bleaching powder which is not carefully kept, a portion of the chlorine is driven off by the carbonic acid of the air.

* The determination of the available chlorine in bleaching powder

is performed by making up a weighed quantity of the latter to one litre with water and allowing the solution to stand till it becomes clear. The solution is then allowed to run from a burette into a measured solution of sodium arsenite, which is obtained by dissolving arsenic trioxide in sodium bicarbonate. The anion of arsenious acid, AsO_3''', is converted into that of arsenic acid by the oxygen of the hypochlorite : $AsO_3''' + ClO' = AsO_4''' + Cl'$. One mole of arsenious acid, therefore, corresponds to one combining weight of oxygen, or two combining weights of chlorine, which are required for the formation of one mole of hypochlorosion. The end of the reaction is ascertained by bringing a small trace of the liquid on a piece of paper containing potassium iodide and starch[1]; so soon as the arsenious acid is oxidised and the smallest excess of hypochlorite is present, a blue spot is produced from the liberation of iodine from the potassium iodide. In the case of such a "spot test," the end is most quickly attained by first making a rapid approximate experiment and then repeating the analysis, running in most of the liquid at once, so that only the last portion has to be added in drops and tested.

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[1] A difference would be proved if it could be shown that differences of any kind, *e.g.* in the heat of solution, existed between bleaching powder and a mixture of the two salts. Calcium hypochlorite, however, is scarcely known in the pure state.

Like all hypochlorites, bleaching powder is an unstable compound (p. 211), which passes spontaneously into the more stable form, calcium chloride and oxygen, and whose period of existence is therefore limited. Pure, dry bleaching powder is stable enough for its technical application, but there are catalysers which greatly accelerate the decomposition. Such substances are, more especially, the higher oxides of the heavy metals, cobalt and nickel; on adding a little of a cobalt salt to a concentrated solution of bleaching powder, whereby the metal is at once converted into the corresponding oxide, the evolution of oxygen commences and becomes very energetic on slightly warming. The reaction, therefore, $2ClO' = 2Cl' + O_2$, which of itself takes place very slowly, is converted into a rapid one.

Calcium Bromide and Calcium Iodide are very readily soluble salts, still more deliquescent than the chloride, and have no special application. The iodide is characterised by the fact that it very rapidly becomes brown in the air owing to the liberation of iodine. This is due to decomposition by the carbonic acid of the air, by the action of which a trace of hydriodic acid is formed which is forthwith converted by the atmospheric oxygen into iodine and water. The reason why this process takes place so much more readily in the case of calcium iodide than, *e.g.*, with potassium iodide, is that the calcium carbonate which is formed has, by reason of its slight solubility, no action on free iodine, whereas potassium carbonate would partly convert free iodine into iodide and iodate, *i.e.* would to a certain extent hinder the formation of free iodine.

Calcium Fluoride.—Unlike the other halogen compounds of calcium, calcium fluoride, CaF_2, is very difficultly soluble in water.

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[1] Almost all writing paper already contains starch.

The salt forms a widely distributed mineral which is known by the name of fluor-spar; it crystallises in cubes and in other forms of the regular system, is colourless and transparent in the pure state, but, owing to the presence of impurities, is generally coloured in various bright tints.

The name fluor-spar is derived from its application in metallurgical work for rendering the slags which are there formed readily fusible. This action depends on the general fact that the freezing point of a liquid is depressed by the solution in it of foreign substances; it is, of course, of no importance for this action whether the freezing point is at 0° or at 1000°. The element fluorine, also, has received its name on account of its preparation from fluor-spar.

* Another name which is connected with this is *fluorescence*, which is used to designate the property possessed by certain substances of changing incident light into light of (generally) greater wave-length. This property was first investigated with some degree of thoroughness in the case of certain kinds of fluor-spar, but the property is a very frequent one, and is more strongly developed in some other substances than fluor-spar.

Fluor-spar is the most important starting substance for obtaining hydrofluoric acid and the other fluorine compounds. Even at the present time large quantities of it are used directly for the purpose of etching glass; the salt is mixed with concentrated sulphuric acid, and the articles to be etched are exposed to the action of the vapours of hydrofluoric acid which are evolved.

Calcium Nitrate, $Ca(NO_3)_2$, is being unceasingly formed through the activity of the nitrifying bacteria (p. 461) in the soil, since calcium is the most widely distributed of the salt-forming elements which have here to be taken into account. In localities where the formation of nitrate is abundant, such as in the neighbourhood of cow-houses, the anhydrous salt sometimes crystallises out during dry weather on the stone walls in the form of thin needles which have almost the appearance of mould. As a rule, no great accumulation of the salt occurs in the soil, since the nitrates formed are at once taken up by plants.

The pure salt is very soluble in water, and, at medium temperatures, crystallises with $4H_2O$. It, also, is capable of forming a fairly large number of different hydrates.

Calcium Sulphate, $CaSO_4$, is difficultly soluble in water; it occurs very widely distributed in nature, and, after calcium carbonate, is the most abundant salt of calcium. It occurs in two forms. It occurs most frequently as gypsum, in monoclinic, sometimes very large and transparent crystals with two moles of water of crystallisation; and more rarely as anhydrite, in anhydrous, rhombic crystals. The solubility of these two forms is different, gypsum being more difficultly soluble than anhydrite. In the presence of water, therefore, the latter is the less stable form and changes into gypsum; in this case, also the presence of a "nucleus" of the more stable form has an essentia influence on the process.

The solubility of gypsum amounts to about 2 gm. per litre; as the temperature rises, the solubility first increases, reaches a maximum at 40°, and then decreases. On being heated, gypsum loses $\frac{3}{4}$ths of its water of crystallisation fairly readily, and the transparent crystals are thereby converted into a chalk-white powder, which has a manifold application under the name of *plaster of Paris*. This depends on the fact that the powder again takes up its water of crystallisation in contact with water the long needles of the crystallised gypsum are thereby again formed, and these, intergrowing with one another, form a compact mass. This property is made use of for moulding objects for use and works of art, for plastering walls, for bandages in surgery, etc. The hardening of plaster of Paris which has been slaked with water takes place in about a quarter of an hour, and is accompanied by a feeble but appreciable rise of temperature.

* If in the dehydration process the gypsum has been heated too strongly, it does not again harden, or does so only very slowly, so that it can no longer be used. Such gypsum is called "dead burnt." The cause of this behaviour has not yet been thoroughly investigated. From the fact, however, that the dehydrated gypsum, when it is in a condition to be used, still contains about a quarter of its water of crystallisation, it can be presumed that dead burnt gypsum does not harden for the reason that the "nuclei" for the formation of new crystals of gypsum, viz., undecomposed particles of gypsum, are then no longer present. The following experiment illustrates this view. If effloresced Glauber's salt, in which "nuclei" are still present (p. 485), is mixed with a little water, the mixture at once hardens to a solid mass of Glauber's salt; but if the powder is previously heated, so that the nuclei are destroyed, and is then mixed with water, avoiding the introduction of nuclei from without, no solidification occurs, but a paste is formed consisting of a saturated solution of the anhydrous salt along with undissolved substance.

The naturally occurring anhydrite is generally found along with common salt as the residue from the evaporation of former seas. Experiment also shows that gypsum passes into anhydrite in presence of a saturated solution of common salt at 125°. This is due to the fact that the vapour pressure of the water from gypsum plus anhydrite is greater than that from the saturated solution of common salt. If, therefore, a mixture of gypsum and some anhydrite be placed along with a saturated solution of common salt in an enclosed space, water must pass off from the gypsum and be taken up by the solution of salt. If, therefore, under these circumstances, the two substances are not in equilibrium, neither can they be so when they are in direct contact, *i.e.* in the presence of a saturated solution of common salt calcium sulphate cannot be deposited and remain as gypsum, but must separate out as anhydrite or be converted into this.

* On the other hand, dehydrated gypsum takes up water from a solution of common salt at the ordinary temperature; the two vapour pressure curves must, therefore, cut one another at an intermediate point. In the case, however, of the naturally occurring residues of evaporation, the mother liquors always contain large amounts of magnesium chloride and have, therefore, a much smaller vapour pressure than the pure solution of common salt, so that the above discussion can be applied to these mother liquors even at a lower temperature.

Intermediate between gypsum and anhydrite there exists another hydrate, $CaSO_4 . \frac{1}{2}H_2O$, which is formed when the dehydration is carried out less thoroughly.

Calcium Sulphide.—The crude calcium sulphide, CaS, has already been met with as a by-product in the manufacture of soda by the Le Blanc process (p. 490). It can be obtained in the pure state by the reduction of calcium sulphate with charcoal or hydrogen, or by strongly heating lime in an atmosphere of sulphuretted hydrogen or of carbon disulphide.

The salt is a whitish-yellow, scarcely fusible mass, which is only very slightly soluble in water, but is decomposed on being warmed for some time with it, calcium hydrosulphide passing into solution, and calcium hydroxide remaining behind: $2CaS + 2H_2O = Ca(HS)_2 + Ca(OH)_2$. This process corresponds exactly with the decomposition which the soluble sulphides of the alkali metals experience (p. 460), only that in this case the hydroxide formed is deposited on account of its slight solubility.

The above-mentioned calcium hydrosulphide, $Ca(HS)_2$, or the acid calcium salt of sulphuretted hydrogen, is known only in solution; solutions containing a fairly large quantity of it can be obtained by passing sulphuretted hydrogen into water in which calcium sulphide is suspended. On concentrating the solution, sulphuretted hydrogen passes off along with water vapour, and only calcium sulphide, or its products of decomposition, is obtained.

If calcium sulphide is heated with sulphur and water, the compounds CaS_4 and CaS_5 are formed, which dissolve in water with an orange-red colour; compounds with two or three combining weights of sulphur are not known. Milk of sulphur (p. 256) is prepared by decomposing these polysulphides of calcium with acids.

The moist calcium sulphide, such as was obtained as a residue in the older process of soda manufacture, readily oxidises in the air, polysulphides of calcium, and, subsequently, calcium thiosulphate, being thereby formed. By decomposing the mass when it is in this state with sodium carbonate or sodium sulphate, sodium thiosulphate can be obtained. The purifying material containing calcium sulphide which is obtained in gas-works, is also used for the same purpose. Fresh moist soda-waste can be converted into calcium carbonate and sulphuretted hydrogen by means of carbon dioxide; the sulphuretted hydrogen on being burned again yields sulphur or sulphur dioxide. On thi depends a method of "sulphur regeneration" (p. 491).

Some specimens of calcium sulphide, after having been illuminated have the property of shining with their own light, or of *phosphorescing* It has, however, been found that this property does not belong to th calcium sulphide itself, but is produced by the presence of quite smal amounts of the sulphides of some heavy metals (bismuth, manganese) Such material has a certain technical importance as "phosphorescen paint," for applying to such objects as it is desired to render visible i the dark.

Calcium Phosphate.—The salts which phosphoric acid form with calcium are of great importance for organic life. On the on hand, the bones of the vertebrate animals consist chiefly of calciun phosphate; on the other hand, the naturally occurring calcium phosphates are the most important source of the phosphoric acid whicl is employed for manurial purposes, and which is indispensable for high cultivation of the soil.

The normal or saturated calcium phosphate, $Ca_3P_2O_8$, occurs i nature as *phosphorite*, in masses which are of organic origin. The sal is obtained as a white, amorphous precipitate which shows no tendency to become crystalline, by the precipitation of a calcium salt with solution of sodium phosphate which has been rendered alkaline When dry, it is a white, very difficultly fusible powder. The residue *bone-ash*, which is left on destroying the organic matter of bones by burning in air, consists essentially of impure tricalcium phosphate.

Tricalcium phosphate is practically insoluble in water, but readily dissolves in dilute and weak acids, *e.g.* acetic acid. This ready solubility in acids is due to the tendency of the trivalent ion PO_4''' to unite with hydrion and to pass into the divalent HPO_4'' (p. 363). In the soil, also, where this salt either is already present or is at once formed on manuring with soluble phosphates, it is gradually attacked by the carbonic acid and made available for the plants. This is seen from the fact that tricalcium phosphate dissolves much more abundantly in water containing carbonic acid than in pure water.

When a normal calcium salt is mixed with a solution of ordinary disodium phosphate, an amorphous precipitate is at first deposited the composition of which approximates to that of the normal salt On standing and more quickly on slightly acidifying, the precipitate is converted into small, lustrous crystals of dicalcium phosphate $Ca_2H_2P_2O_8 = 2CaHPO_4$, which are anhydrous when formed at moderately high temperatures; the crystals which are formed in the cold contain $2H_2O$.

This salt does not dissolve unchanged in water, for in contact with much water it becomes turbid and yields a liquid with an acid reaction, along with an amorphous residue whose composition approximates to that of the normal salt. This reaction seems to depend on the very slight solubility of the normal salt, in consequence of which the ions present unite to form that salt, while a corresponding excess of hydrion is produced in the solution and causes the acid reaction. The reactions which occur can be represented by the equation $3Ca^{\cdot\cdot} + 2HPO_4'' = Ca_3P_2O_8 + 2H^{\cdot}$, but it must be kept in view that this transformation affects only a part of the substance present, and that we are dealing with a chemical equilibrium which is altered by the temperature and concentration.

Finally, from more strongly acid solutions, the monocalcium phosphate, $CaH_4P_2O_8$, crystallises out in lustrous crystals which dissolve in much water apparently unchanged; when, however, less water is taken amorphous salt containing more calcium is deposited, and a solution with a strongly acid reaction is formed. This salt is the chief constituent of the artificial phosphoric acid fertiliser known as superphosphate. The latter is prepared by decomposing normal calcium phosphate with sulphuric acid according to the equation $Ca_3P_2O_8 + 2H_2SO_4 = CaH_4P_2O_8 + 2CaSO_4$.

Thomas slag, which is a by-product obtained in the manufacture of ron, being formed in the process of removing the phosphorus contained n pig-iron by fusing the latter in presence of oxidising substances and of lime, consists essentially of normal calcium phosphate. The lag contains an excess of lime, and in moist air rapidly disintegrates, therefore, to a fine powder which is sufficiently susceptible to decomposition by water and carbonic acid. It is, therefore, used as a ertiliser without being previously treated with acid.

Apatite is a mineral crystallising in hexagonal prisms, and is a double salt of calcium phosphate and calcium fluoride, or chloride, having the formula $Ca_5(PO_4)_3Cl$ or $Ca_5(PO_4)_3F$. We can imagine hese as being composed in such a way that the hydrogen of three ombining weights of phosphoric acid and of one halogen hydride are eplaced by calcium. Since one combining weight of calcium replaces wo combining weights of hydrogen, the nine combining weights of hydrogen present from the phosphoric acid cannot be replaced without emainder by the divalent calcium. Five combining weights of calcium nter, and the tenth unit is satisfied by the monovalent halogen, fluorine, or chlorine.

If acid calcium phosphate is heated, it loses water and passes into *alcium metaphosphate*, $Ca(PO_3)_2$. This salt is of importance as the tarting substance in the preparation of phosphorus, which is obtained y strongly heating this salt with charcoal. There then occurs the eaction $3Ca(PO_3)_2 + 10C = 4P + Ca_3(PO_4)_2 + 10CO$, and the phoshorus vapour which is formed passes, on cooling, into white phoshorus. At the present day, however, phosphorus is no longer prepared in this way, but in the electric furnace, a mixture of calciu orthophosphate, quartz sand, and charcoal being probably employe Details of this process are, however, not yet known.

Calcium Acetate.—A certain interest attaches to the calciu salt of acetic acid (p. 398), from the fact that it is an intermedia product in the preparation of pure acetic acid from the crude produc wood vinegar, formed in the dry distillation of wood. In order separate acetic acid from the other, non-acid substances present, it converted into a salt, and for this purpose lime, being the cheape base, is employed. The solution of the crude salt is evaporated dryness and rather strongly heated in order to destroy a large porti of the impurities present. The salt is placed on the market in th form, and is worked up for acetic acid and other substances, in speci works.

Calcium acetate has the composition $Ca(C_2H_3O_2)_2$, and is a sa which is very readily soluble in water, and which crystallises wi $1H_2O$. Acetic acid is liberated from it by sulphuric acid.

If calcium acetate is heated with excess of lime, methane formed: $Ca(C_2H_3O_2)_2 + Ca(OH)_2 = 2CH_4 + 2CaCO_3$ (p. 398). Heate without the addition of lime, it yields another substance called *aceton* according to the equation $Ca(C_2H_3O_2)_2 = CaCO_3 + C_3H_6O$; this is colourless, volatile liquid, and has a manifold application in chemic industry.

Calcium Oxalate.—It has already been mentioned that th calcium salt of oxalic acid, CaC_2O_4, is used for the detection an precipitation of calcion. Calcium oxalate is exceedingly slightl soluble in water, and is at once formed when oxalanion and calcio come together in solution. The precipitate is practically insoluble i acetic acid, but is soluble in dilute hydrochloric and nitric acids; i fact, in all strong acids which form soluble calcium salts.

The reason of this is that oxalic acid is an acid the strength, (electrolytic dissociation, of which lies between that of hydrochlor acid and of acetic acid. If calcium oxalate is brought into conta with water, a very small quantity of the precipitate dissolves. acetic acid is added to the liquid, it contains such a small amount free hydrion that only an extremely slight change takes place in th chemical equilibrium, in such a sense that quite a small quantity the oxalanion unites with hydrion to form undissociated oxalic acid, the monovalent hydro-oxalanion, C_2O_4H'; the consequence is a ver small increase in the amount of salt passing into solution. Since, it is, the solubility of calcium oxalate is very slight, this increase is no account analytically.

The case is different when a strongly dissociated acid, like hydr chloric acid, is added. A large amount of hydrion is then introduc into the solution, and, accordingly, a comparatively large amount oxalanion, C_2O_4'', disappears, owing to the formation of HC_2O_4' an

$H_2C_2O_4$, and must be replaced by more calcium oxalate passing into solution. Accordingly, much more of the precipitate will be dissolved, and with sufficient amount of hydrochloric acid the whole precipitate passes into solution.

For this reason, in precipitating calcion with oxalanion, one does not use a solution of free oxalic acid, whereby the detrimental hydrion would be introduced into the solution, but ammonium oxalate is employed. If the solution itself is strongly acid, the excess of hydrion can be removed by addition of sodium acetate; acetanion, being the ion of a weak acid, unites with the greater part of the hydrion to form undissociated acetic acid, and only a harmless amount of hydrion is left behind.

According to the temperature employed, the precipitate of calcium oxalate contains various amounts of water of crystallisation, and cannot, therefore, be weighed as such in the quantitative determination of calcium. It is, therefore, heated either gently to convert it into calcium carbonate ($CaC_2O_4 = CaCO_3 + CO$), or, since some calcium oxide can thereby be readily formed, it is better to heat it to a bright red heat, whereby it is completely converted into calcium oxide.

Calcium oxalate is also found as a constituent of certain urinary calculi and very widely distributed in almost all plants; in the cells of the latter the comparatively large, transparent octahedra of hydrated calcium oxalate, which have the appearance of an envelope, can be readily recognised under the microscope.

Calcium Carbide.—If carbon acts on lime at a very high temperature, there occurs the reaction $CaO + 3C = CaC_2 + CO$. The compound CaC_2 which is formed, is called *calcium carbide*, and has been manufactured for some years in very large quantities for conversion into acetylene (p. 405).

The reaction is carried out in the electric furnace, but the process has nothing to do with electrolysis, the current serving only to produce the requisite high temperature, and to yield the large amounts of energy which the reaction requires. In Fig. 109 an experimental electric furnace is represented, formed simply of refractory stone.

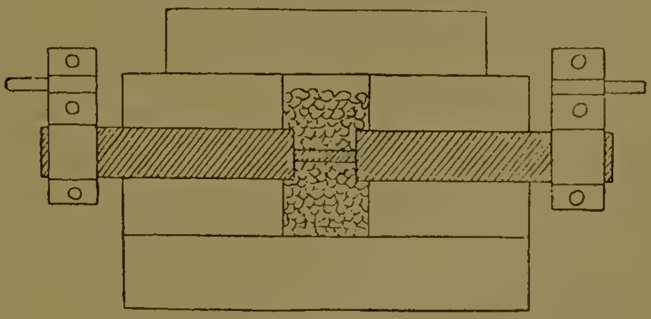

Fig. 109.

Pure calcium carbide forms almost colourless crystals. The commercial product appears as a black-grey mass of irregular lumps, having the characteristic smell of phosphoretted hydrogen, which, however, is due only to impurities. Its density is 3·22, and it does not melt below a white-heat.

The most important reaction of the carbide is that it is decon posed by water with formation of calcium hydroxide and acetylen $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$. In this reaction a considerab amount of heat is developed, so that if water is allowed to come int contact with a comparatively large quantity of carbide, the ten perature can rise to a red-heat. The acetylene is, however, decon posed under such conditions, and a poorly luminous gas is obtaine Those acetylene generators, therefore, are the best in which th carbide falls into a comparatively large quantity of water, or i which the rise of temperature is otherwise avoided.

* The problem of making an automatic acetylene generator, whic appears capable of simple solution on the principle of the apparatu described on p. 86, has in reality turned out to be very difficult. Thi is due, on the one hand, to the fact just mentioned, and on the othe hand, to the fact that calcium carbide reacts powerfully even wit water *vapour*, so that the so-called *after-evolution* of gas, *i.e.* a consta evolution of gas even when the apparatus should be at rest, is difficul to avoid.

* The detrimental effect of moderate heat on acetylene can b easily shown by allowing the gas to pass through a horizontal tub before entering the burner. So long as the tube is cold, the flam burns very brightly, but so soon as it is heated even to a dark re heat, the flame becomes almost non-luminous, and charcoal is deposite in the tube.

Calcium Silicate and Glass.—Silicates of calcium occur in th pure state in nature, forming unimportant minerals which have but slight distribution (wollastonite). Combined with other silicates, how ever, calcium silicate is a very frequent constituent of the naturall occurring minerals.

As a chemical product, also, calcium silicate itself is of no import ance, but is of great importance when mixed with the silicates of th alkali metals. These mixtures constitute *glass*, the well-known resist ant and transparent material which finds an application in all depart ments of daily life, in the manufactures, in art, and in science.

Glass is a mixture of potassium or sodium silicate and calcium silicate. This is the composition of ordinary window-glass or o glassware. For special purposes, still other metal oxides are used and also phosphoric and boric acids in place of silicic acid.

The chemical composition of good glass agrees approximately with the formula $A_2CaSi_6O_{14}$, where A signifies potassium or sodium or both Ordinary glass, however, generally contains less silicic acid, since it i then more easily fusible.

Glass is amorphous, as is shown by its isotropic nature and the absence of a definite melting point. In certain glasses there is a tendency for some portions to separate out in the crystalline state this is known as "devitrification," and it is endeavoured to avoid this condition by a suitable change in the proportions of the mixture. All the same, devitrification occurs in the case of almost all glasses when they are maintained for a long time at a temperature near the point of softening, but with good glass the process takes place with extreme slowness.

Whilst alkali silicate is fairly readily dissolved by water, glass is very resistant to this. It is attacked least of all by acid solutions; pure water attacks it more strongly, and alkaline solutions most strongly of all. By exposure for some time to the action of steam, the surface of glass vessels becomes less easily attacked. Moreover, the resistance of the glass depends very largely on its composition; it is all the less the poorer the glass is in silicic acid and the richer it is in alkalis. Further, the remarkable behaviour has been discovered that glass which contains potash or soda *alone*, is much more resistant than glass which contains both alkalis together.

* By reason of the inclination towards economy of fuel, it had formerly become a custom in glass-works to manufacture a readily fusible glass, rich in alkali, so that the bad and small resistant character of such glasses became a source of distress. The scientific investigations which were in consequence carried out, some of which have been mentioned above, at once led to a suitable adjustment of the factors which must be taken into account for manufacturing purposes, and at the present time there is produced at many places, and especially at Jena, a glass for apparatus which is considerably superior in quality to the best sorts of glass previously made.

The action of water on glass consists in free alkali and alkali silicate passing into solution, a hydrated silicate containing less alkali being left. This action increases very rapidly with rising temperature, and above 200° no glass withstands the action of water.

In the manufacture of glass, one starts with silicon dioxide (quartz sand), potassium or sodium carbonate, and calcium carbonate. The components, mixed in the proper proportions, are first maintained for some time at a moderate red heat; the silicates are thereby formed, but no fusion, only sintering, occurs. This is done in order that the arbon dioxide may escape without the mass being thrown out of the vessels by the evolution of gas. The "frit" is then fused at a higher emperature, and is maintained at such a temperature for a sufficiently ong time to allow the gas bubbles to escape, and the undissolved ieces of the mass to sink to the bottom.

If the glass is to be worked up by pouring into moulds, it may be sed in the above condition of a thin liquid. Generally, however, the glass is "blown," and for that purpose it must be rendered more viscous by lowering the temperature. The blowing of glass is a haping of it with the help of *surface tension*. A certain amount of he liquid glass is taken up with an iron tube, the "blow-pipe," and s blown up like a soap-bubble. The fundamental form which is obtained is therefore a hollow sphere; under the action of gravity, c centrifugal force, and especially by suitably heating and coolin different parts of the object, very various forms can be produced.

For many pieces of apparatus, especially when small and compl cated, the glass is worked *before the blow-pipe*, after it has been brough into the form of tubes of various thickness and width in the glas works. These tubes are obtained by first blowing a bulb, then fusin an iron rod to a point diametrically opposite to the blow-pipe an rapidly separating the two points of attachment from one another. very elongated ellipsoid is formed, the middle portion of which doe not deviate materially from a cylinder. In working before the blow pipe, the same aids are employed as in the works, viz., surface tensio and suitable heating.

* Moulded objects must be "annealed," and this must be all th more carefully done the thicker and larger these objects are. Th annealing consists in allowing the temperature of the glass to sin only very slowly. Quickly cooled glass contains internal strain which arise in the following manner. In rapid cooling, a low tem perature is soon established at the surface, and the outermost laye solidifies while the interior is still very hot. The external volume o the lump corresponds, therefore, to the volume possessed by th interior portion at the high temperature; when the mass has becom quite cold, the interior tends to contract, and thereby exerts on th outer layer a pressure which is directed inwards. In the case of thic glass which has been quickly cooled, this pressure is so great that i the surface is slightly scratched, the mass suddenly flies into man pieces; this can be seen with "Rupert's drops," which consists of glas treated in the above manner. If, however, the cooling is performe slowly, the different parts of the mass have always about the sam temperature, and strains cannot be produced.

Pieces of a regular shape, *e.g.* cylindrical tubes, generally do not require to be annealed, because the strains are distributed symmetrically, and under certain conditions can then even become useful.

Glass consisting of pure calcium and alkali silicate is colourless. For cheaper kinds, less pure material is used, and the iron, which is seldom absent, imparts the well-known black-green or brown colour to the glass, as is seen in the case of bottle-glass. In the place of sodium carbonate also, the cheaper sodium sulphate is frequently employed; charcoal is then added, so that sodium sulphite is formed, which is more readily converted into silicate by the silicic acid. Such glass generally contains some sodium sulphate or even sodium sulphide, and under certain circumstances these can give rise to considerable errors in chemical operations.

Coloured glass is obtained by the addition of various metallic oxides. Thus, cobalt gives blue; copper oxide and chromium oxide, green; iron oxide, yellow to brown; manganese dioxide, violet glass.

Further, glass has the remarkable property of dissolving various metals in the colloidal state. Very intense colorations are then produced; dark red with copper or gold, yellow with silver. Charcoal also dissolves in melting glass, and imparts to it an intense yellow-brown colour.

Milk glass is prepared by adding calcium phosphate (bone-ash) or tin dioxide, which do not dissolve in the glass, and therefore give it a white and opaque appearance.

Combining Weight of Calcium.—In spite of the great importance of this number, which comes into account in all mineral and water analyses, a sufficiently exact knowledge of it has only recently been obtained; the combining weight has been found to be Ca = 40·1, a somewhat higher number than that which was long used, viz. 40·0.

CHAPTER XXIV

MAGNESIUM

General.—Magnesium bears the same relation to calcium as sodium does to potassium. This relation finds expression not only in th values of the combining weights, but also in the similarities to th other members of the group. This is particularly well seen in the fac that magnesium is of more frequent occurrence than calcium, and that in its properties, it differs from calcium more than the latter does fror the corresponding elements of higher combining weight, strontium an barium.

That an elementary metal is present in the magnesium salt, wa regarded by Davy as indubitable from the time that the correspondin fact was recognised in the case of potassium and sodium. Bunsen however, was the first to prepare the metal itself. He obtained it b the electrolysis of the fused chloride.

* The electrolysis can be performed in the lecture by employin fused carnallite as electrolyte and using the apparatus represente in Fig. 110. The partition and the prolongation of the crucible are of asbestos mill-board the cathode is a piece of iron wire, and th anode a thin arc-carbon. The strength of th current is about 3–10 amperes.

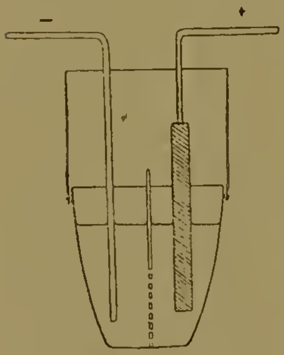

Fig. 110.

Magnesium is now manufactured in ver large amount by electrolysis, and is used fo various purposes. It is a white, rather tough metal, which keeps fairly well in the air; it i scarcely attacked by cold water, but in boilin water it slowly evolves hydrogen. In dilut acids it very rapidly dissolves, with energeti evolution of hydrogen. It melts at about 750°, and volatilises at bright white-heat.

Heated in the air, magnesium burns with a very bright, whit flame, which is largely made use of. For example, instantaneou photographs can be easily taken by magnesium light. For thi purpose magnesium is used in powder form, and is either blown through a flame or is mixed with potassium chlorate or perchlorate, sometimes with potassium permanganate, and ignited.

* The former method has the advantage that comparatively little metal is required, especially when pure oxygen is used instead of air for blowing it; but it has the disadvantage that the flash lasts for a comparatively long time, abont 0·3 second. The second method requires larger quantities of magnesium, but the flash lasts only 0·1 second, or less. The last mentioned mixture, however, is rather dangerous, as it readily explodes; it ought not, therefore, to be prepared in large quantity.

* Magnesium is also used for other purposes where a bright, transient light is required; in such cases the magnesium is generally burned in the form of ribbon in specially constructed lamps. Magnesium is also used for adding to fire-works.

Magnesium is an exceedingly effective reducing agent at a high temperature. Silicon, boron, and most of the other metals can be obtained by heating their oxygen compounds with magnesium powder, the latter thereby passing into its oxide, MgO.

Magnesion.—Like the other elements of this group, magnesium forms only one kind of ion, viz. divalent magnesion $Mg^{\cdot\cdot}$. This is colourless, and can be detected by means of a number of precipitations. Its heat of formation from the metal amounts to 456 *kj.*

Of its special properties, it may be mentioned that it forms with hydroxidion a very difficultly soluble hydroxide, which is precipitated from solutions containing magnesion by the addition of dissolved hydroxides of the alkali and the other alkaline earth metals. For the detection and determination of magnesion, ammonium magnesium phosphate, $MgNH_4PO_4$, is chiefly used; this is deposited as a hydrated, distinctly crystalline precipitate on adding phosphanion along with ammonia to a solution containing magnesion. A mixture of sodium phosphate and ammonia is generally employed. The other alkaline earth metals, as well as all heavy metals, must have been previously removed from the solution, as is, indeed, customarily done in the regular course of analysis.

Powerful physiological or medicinal actions are not possessed by magnesion, but it has a distinctly bitter taste. It does not play any pecial rôle in the animal organism, although, on account of its frequent occurrence in the earth's crust, it is generally present in it.

Magnesium Hydroxide and Magnesium Oxide.—Difficultly oluble magnesium hydroxide immediately separates out as a white, omewhat gelatinous precipitate from solutions in which magnesion nd hydroxidion come together. Although difficultly, it is still appreciably soluble in water, for it produces distinctly blue marks on moistened litmus paper. In accordance with known laws (p. 440), he solubility is less in solutions containing hydroxidion. The presence of magnesion has the same effect, if new compounds are no formed.

This seems to be contradicted by the fact that magnesia dissolve to an appreciable extent in ammonia, and abundantly in any ammoniu salt, *e.g.* ammonium chloride. The explanation of this is, however, a follows. Ammonia is a slightly dissociated base; when, therefor ammonion and hydroxidion come together in solution, the greater pa of these unite together to form undissociated ammonium hydroxide o ammonia. If, now, water is poured over some magnesium hydroxid a certain small amount of this passes, as already mentioned, into solution, magnesion and hydroxidion being formed. If to this solution fairly large quantity of ammonion is added, this withdraws the greate part of the hydroxidion, and more magnesium hydroxide must pas into solution in order that the solubility product may be reache These fresh amounts of hydroxidion which go into solution are als removed, and this process goes on until either all magnesium hydroxid is dissolved or the equilibrium between hydroxidion and ammonion i attained.

From this it is also seen why ammonium salts exert a so muc more powerful solvent action than free ammonia. In the first place, th latter is much less dissociated, and contains, therefore, comparativel little ammonion; and, in the second place, it contains hydroxidion, an thereby diminishes the solubility of magnesium hydroxide.

This behaviour of magnesium hydroxide is an important characteristic in analysis.

Magnesium hydroxide, on being heated, very readily loses wate and passes into the anhydride, magnesium oxide or *magnesia*, MgO This is a white, very light powder, which is generally prepared b heating basic magnesium carbonate, to be mentioned later, and i therefore called magnesia usta, or calcined magnesia. It is used i medicine as a mild alkali.

Magnesia withstands very high temperatures without melting, an is therefore used for lining furnaces in which high temperatures ar produced. The strongly illuminating power of burning magnesium i due to the same fact.

On being mixed with water, magnesia which has been feebl heated takes up some of the latter and forms magnesium hydroxide with slight evolution of heat. When strongly heated, magnesi diminishes in bulk, becomes crystalline, and loses its power of unitin with water.

For technical purposes, magnesia is obtained either by heating th naturally occurring magnesium carbonate (which see), or by decomposing magnesium chloride, which is formed in large quantities as a by-product in the preparation of potassium chloride from carnallite, by means of lime.

Magnesium Chloride is very readily soluble, and deliquesces i the air; from its very concentrated solutions it crystallises in the cold with $6H_2O$. The hydrated crystalline salt cannot be dehydrated by heating without undergoing decomposition, for it loses hydrogen chloride, and magnesium oxide or a basic chloride is formed: $MgCl_2 + H_2O = MgO + 2HCl$. This reaction is made use of on the large scale for obtaining hydrochloric acid; in recent times this has become of greater importance from the fact that the formerly very abundant source of hydrochloric acid constituted by the Le Blanc method of manufacturing soda is beginning to fail. For this reason magnesia is used even in those alkali works which use the ammonia process for the decomposition of the ammonium chloride which is formed (p. 492), because magnesium chloride can be much more easily decomposed by steam than calcium chloride.

Magnesium chloride forms double salts with potassium or ammonium chloride, of which that with potassium chloride, $MgCl_2 . KCl . 6H_2O$, called *carnallite*, is the most important naturally occurring potassium salt. It is found in large quantities at Stassfurt and in other parts of Middle and North Germany, and is separated into its components by crystallisation in the heat. The rather complicated equilibrium relations which exist in such solutions, show that in general it is most expedient to work at high temperatures. For example, if carnallite is heated without the addition of water, it liquefies at 176°, and deposits the greater part of the potassium chloride in the solid state; on cooling down, almost all the rest of the potassium chloride crystallises out as carnallite, and the magnesium chloride remains in the mother liquor.

The greater part of the magnesium chloride produced in the manufacture of the potash salt finds no application at present, but is turned into the river channels. It is to be desired that some technically practicable means may be discovered to put an end to this, from various points of view, detrimental waste.

Magnesium Sulphate, $MgSO_4$, is a substance well known under the name of Epsom salts; it has a bitter taste, due to magnesion. It usually crystallises in rhombic crystals with $7H_2O$. It can, however, occur in a number of other forms containing from $12H_2O$ to $1H_2O$, according to the temperature. Mono-hydrated magnesium sulphate occurs in the Stassfurt salts as kieserite. Dissolved magnesium sulphate is a constituent of many mineral waters,[1] to which it imparts a bitter taste, and which are known as magnesia waters. The action of Epsom salts in the intestine is quite similar to that of Glauber's salt (p. 482).

Magnesium sulphate unites with potassium or ammonium sulphate to form double salts of the formula $MgSO_4 . K_2SO_4 . 6H_2O$. The potassium compound has the mineralogical name schoenite, and is used as a potash manure.

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[1] The name Epsom salts is derived from the occurrence of this salt in the mineral waters at Epsom.—Tr.

By *double salt* there is understood a crystalline compound of severa normal salts with one another. This combination exists essentially only in the solid state, for the aqueous solutions of these double salts exhibit exactly the same reactions as belong to the ions of the single salts, and no reactions which could belong to any new ions. The determination of the molar weights of these aqueous solutions, also, shows that no combination between the single salts exists to an appreciable extent; for the depression of the freezing point, for example, is equal to the sum of the depressions which are caused by the single salts under the same conditions.

This holds in the first instance for dilute solutions. In concentrated solutions certain phenomena point to combination existing in them to a certain, although not large, extent.

As a rule, double salts are less soluble in water than the components. If the difference is great, these double salts readily crystallise from solutions in which the components are brought together. If, however, the solubilities are of the same order, it depends on the temperature and the relative amounts whether crystals of the double salt or of one of the components are obtained on concentration. In some cases double salts can be obtained only from solutions which contain a large excess of one of the components. This holds, for example, for the crystallisation of carnallite, which is formed only from solutions containing a large excess of magnesium chloride.

Double salts are generally so constituted that the single salts have *one* ion, either the cation or the anion, in common. Double salts with different cations and anions do indeed occur, but they are more seldom. A double salt of this nature is kainite, $KCl . MgSO_4 . 3H_2O$, which occurs at Stassfurt.

The *complex salts* must be distinguished from the double salts. Like the double salts, they can be formed by the union of two simple salts, but their reactions in solution differ from those of the latter, which shows that new substances (ions) are formed. Further information concerning this interesting class of compounds will be given later, when we come to describe some complex salts (*v.* Chap. XXVII.). The alkali and alkaline earth metals do not form any complex cations.

The *isomorphous mixtures*, also, must be distinguished from the double salts. They arise by the crystallisation of isomorphous salts from a common solution; thus, for example, a mixed solution of rubidium and potassium sulphates, or of sodium sulphate and sodium selenate, deposits crystals whose composition also appears as the sum of the two components. These mixtures differ from the double salts in the fact that their components are not, or are only accidentally, present in combining proportions, and in the fact that their composition varies continuously with the composition of the solution from which they are deposited. Their composition, therefore, cannot be represented by an ordinary chemical formula, but only by one with indefinite or continuously varying coefficients. They are usually written in the form $(K,Rb)_2SO_4$, and $Na_2(S,Se)O_4 . 10H_2O$, the elements which replace one another in indefinite proportions being placed in brackets and separated by a comma.

The double salts, however, are always compounded in combining proportions, and can, therefore, be represented by a chemical formula with definite, integral coefficients.

Magnesium Carbonate, $MgCO_3$, is a salt very difficultly soluble in water, which occurs in nature in large masses. As a mineral, it is called magnesite, and crystallises in rhombohedra which are isomorphous with those of calc-spar.

When aqueous solutions containing magnesion and carbanion are mixed, a white, gelatinous precipitate is deposited, and carbon dioxide is evolved at the same time. This precipitate is not pure magnesium carbonate, but a varying mixture of carbonate and hydroxide. The higher the temperature and the greater the dilution, the greater is the amount of hydroxide and the less that of the carbonate contained in the precipitate. Washed with water and dried at a low temperature, this basic magnesium carbonate is placed on the market in the form of a light and loose powder, and is used in medicine as a mild alkali. It is called magnesia alba.

* The cause of this reaction is found in the hydrolysis which the carbonates undergo, and in the small solubility of magnesium hydroxide. In the aqueous solutions of calcium carbonate, also, hydrolysis occurs, and the ions HCO_3' and OH' are formed from carbanion, CO_3'', under the action of the water. Since, however, calcium hydroxide is much more soluble than the carbonate, the solubility product of the former is never reached, in spite of the presence of hydroxyl; and although the solution reacts alkaline, it deposits no hydroxide. In the same way, when the ions $Ca^{\cdot\cdot}$, CO_3'', HCO_3', and OH' come together, as happens in the precipitation of a calcium salt with a soluble carbonate, the solubility product of the calcium carbonate is much sooner reached than that of the hydroxide; the precipitate, therefore, in spite of the hydrolysis which occurs, consists of normal carbonate. On the other hand, in the case of magnesium, the solubility product of the hydroxide is, under such conditions, reached about the same time as that of the carbonate.

The normal carbonate can be prepared from the basic salt by suspending the latter in water and passing in carbon dioxide. After some time crystalline crusts of the hydrate, $MgCO_3 + 3H_2O$, are formed. On being treated with much water, especially in the heat, it again passes into the basic hydrate.

Magnesium carbonate forms various double salts with the alkali carbonates. One of these, $MgCO_3 . KHCO_3 . 4H_2O$, is deposited when carbon dioxide, under pressure, is passed into a solution of potassium chloride containing magnesium carbonate in suspension; magnesium chloride is formed at the same time and remains in solution. When this double salt is treated with steam under pressure, it decomposes into potassium carbonate, which passes into solution, and magnesium carbonate, which is deposited; at the same time carbon dioxide escapes. These reactions are made use of for obtaining potassium carbonate from potassium chloride (p. 456).

Another double salt of magnesium carbonate is that with calcium carbonate. This forms enormous rock masses, and in mineralogy is called *dolomite.* The composition is $CaCO_3 . MgCO_3$.

* Formerly, dolomite was regarded as an isomorphous mixture of the two carbonates, especially as these salts are really isomorphous. The uniform composition, however, corresponding to the formula, makes it very natural to suppose that it is a chemical compound; recently, also, it has been proved that dolomite, in spite of the fact that it crystallises in rhombohedra, really belongs to another group of the trigonal system than the two single carbonates, so that it cannot be isomorphous with these, although the forms appear very similar. A further argument against isomorphism is that the properties (*e.g.* the density) of dolomite are not equal to the mean of the properties of the two components, as is the case with true isomorphous mixtures, but differ from this by definite amounts, which is again a characteristic of chemical combination.

* There are numerous varieties of calc-spar which contain magnesium carbonate, and which are as frequent as the varieties of magnesite containing lime. These are true isomorphous mixtures. The amount of admixed substance, however, is never greater than a few per cent. This is connected with the fact that many isomorphous substances cannot crystallise together in all proportions, but only up to a certain limit. This is a phenomenon quite similar to that of the limited mutual solubility of some liquids. Thus, calc-spar can take up a few per cent of magnesite to form an isomorphous mixture, and *vice versa;* the limit of mixing is, however, then reached, and an excess is not possible. In like manner, ether can dissolve a few per cent of water, and water about 10 per cent of ether, but no more.

Magnesium Phosphates.—The compounds of magnesium with phosphoric acid have, in general, neither a theoretical nor a practical interest, except magnesium ammonium phosphate, which has been already mentioned, and which is formed when the requisite ions come together in solution. It is then deposited as a precipitate which is very difficultly soluble in water containing ammonia; it has the composition $MgNH_4PO_4 . 6H_2O$, and is also found naturally as *struvite,* in localities where the conditions of its formation are present. On being heated, it loses ammonia and water and passes into magnesium pyrophosphate, $Mg_2P_2O_7$. In this form the precipitate is weighed. It is very readily soluble in acids, is decomposed by pure water, but can be washed with water containing ammonia without undergoing decomposition. All these properties can be explained by the law of mass action.

As all reagents are reciprocal, phosphanion can be used as a reagent for magnesion just as well as magnesion can be used for phosphanion. For the latter purpose, "magnesia mixture," a mixture of magnesium chloride, ammonium chloride, and ammonia in aqueous solution, is used. When this mixture comes together with phosphanion, the precipitate of magnesium ammonium phosphate immediately separates out, and is then used for the determination of phosphoric acid (*e.g.* in artificial manures).

Of the other anions, that of arsenic acid is the only one that gives a similar precipitate. It is used for the precipitation and determination of arsenic acid. Confusion with phosphoric acid is easily avoided by means of the different behaviour of the original solution towards sulphuretted hydrogen (*vide infra*).

Magnesium Sulphide.—Magnesium sulphide, MgS, is obtained as a yellow-gray mass by strongly heating magnesium metal in the vapour of sulphur. With water, it undergoes decomposition to sulphuretted hydrogen and magnesia: $MgS + 2H_2O = Mg(OH)_2 + H_2S$. For this reason, no magnesium sulphide is obtained by the action of sulphuretted hydrogen on magnesia, or of ammonium sulphide on magnesium salts in solution; but in the latter case, only magnesia is precipitated.

Magnesium hydrosulphide, $Mg(HS)_2$, however, can be obtained in solution by passing sulphuretted hydrogen into water containing magnesium hydroxide in suspension. The magnesia dissolves slowly but abundantly; the liquid which is formed, however, is very unstable, and on evaporation entirely decomposes into magnesia and sulphuretted hydrogen.

* In these reactions we again perceive the same behaviour as in the case of calcium sulphide (p. 521), only with such differences as are caused by the slight solubility of magnesium hydroxide. The decomposability of the sulphur compounds of magnesium is thereby increased, since the precipitated hydroxide, being a solid substance, no longer takes part in the equilibrium, and thus renders a further decomposition in the same sense possible.

The **Magnesium Silicates** are exceedingly widely distributed in nature. *Talc* and *olivine* are anhydrous, *soapstone* and *serpentine* hydrated, silicates of magnesium. Further, magnesium silicate forms a constituent of numerous compound silicates.

Of all the light metals which have to be taken into account, magnesium is the only one whose silicates withstand the action of water and carbonic acid, so that they can be formed afresh under the conditions which prevail at the present time on the earth's surface (p. 421). This is especially true of the hydrated compounds; in the occurrence of serpentine, the slow transformation of the original rock into the new, stable compound can be observed in all stages.

The above mentioned silicates have rather different compositions and, except olivine, contain more silicon dioxide than corresponds t the composition of an orthosilicate. They are distinguished by being of a peculiarly soft and easily worked nature, accompanied by a grea resistance to high temperature, and on this depend their applications They are mostly fairly readily decomposed by sulphuric acid.

Magnesium Nitride.—Magnesium nitride, Mg_3N_2, is obtained a a yellowish, porous mass by heating metallic magnesium to incandescence in nitrogen or ammonia gas. It is decomposed with energy by water, with formation of ammonia and magnesium hydroxide $Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$. In this way ammonia can b obtained from free nitrogen (p. 347); for practical purposes, however the method is still too expensive.

CHAPTER XXV

STRONTIUM, BARIUM, AND BERYLLIUM

General.—Allied to calcium are two metals of higher combining weight which are very similar to calcium in many respects, and which bear the same relation to it as rubidium and cæsium do to potassium. This relation finds expression not only in similar differences of the combining weights, but also in isomorphism, in the relative frequency of occurrence on the earth's surface, and in many other respects. The general summary of these points of agreement will be given at the end of the book.

These two metals are called *Strontium* and *Barium*. They are, it is true, much rarer than calcium, but cannot be designated as rare elements in the same sense as rubidium and cæsium can. On the contrary, they are of sufficiently frequent occurrence to allow of both being characterised as elements as early as the eighteenth century (strontium in 1792 by Hope, barium in 1774 by Scheele), and of their compounds being applied for various purposes.

Strontium has the combining weight 87·61, and occurs in nature chiefly as sulphate and carbonate. Metallic strontium can be fairly readily obtained by the electrolysis of the fused chloride; it can also be obtained by preparing strontium amalgam by the action of sodium amalgam on a concentrated solution of strontium chloride, and distilling off the mercury. It is a yellowish, rather tough metal which nergetically reacts with water even at room temperature.

Strontium forms only the *divalent ion* $Sr^{\cdot\cdot}$, whose solutions are olourless, and whose heat of formation is 501 *kj.*

Strontium Oxide, SrO, is obtained by heating the carbonate or, nore easily, the nitrate. The dissociation of strontium carbonate akes place with much greater difficulty than in the case of calcium arbonate, *i.e.* at the same temperature its dissociation pressure is onsiderably smaller (p. 512). Strontium oxide unites with water to orm strontium hydroxide with great evolution of heat. The latter an also be obtained directly from the carbonate by heating this in a urrent of steam; the decomposition then occurs more easily than without this aid. This is due, on the one hand, to the fact that tl partial pressure of the carbon dioxide is diminished by the stea (p. 513), and, on the other hand, to the fact that in place of tl oxide there is formed the hydroxide, which stands on a lower level.

Strontium Hydroxide is more readily soluble in water tha calcium hydroxide. From the hot saturated solution there ar deposited, on cooling, hydrated crystals of the composition $Sr(OH)_2 \cdot 8H_2O$. The solution exhibits the properties of a strong base, an the determination of the electrical conductivity shows that there is large degree of dissociation into the ions $Sr^{\cdot\cdot}$ and $2OH'$.

Strontium Carbonate occurs as a mineral under the nan *strontianite.* This crystallises in forms of the rhombic system, whic are isomorphous with those of aragonite (p. 511); a form correspon ing to calc-spar is not known. When the ions $Sr^{\cdot\cdot}$ and CO_3'' co together in aqueous solution, strontium carbonate is deposited as white, very difficultly soluble precipitate, which soon passes into tl crystalline state.

Strontianite is used as the initial substance in the preparation other strontium compounds. Other salts can be readily obtained fro it, as the carbonic acid can be expelled by almost all acids. In ord to convert strontianite into strontium hydroxide (an operation whic is of importance on account of the use of the latter in the suga industry), it can be heated in steam. It is also converted int strontium oxide when heated with charcoal: $SrCO_3 + C = SrO + 2C$ This reaction is facilitated by water vapour: $SrCO_3 + C + H_2O =$ $Sr(OH)_2 + 2CO$ (*vide supra*).

Strontium Sulphate, $SrSO_4$, is a white salt which is ver difficultly soluble in water; it occurs naturally as celestine (so-calle from its frequently occurring of a blue colour, due to impurities The mineral crystallises in rhombic forms, and is isomorphous wit anhydrite. From aqueous solution it is obtained as a white pr cipitate when the ions $Sr^{\cdot\cdot}$ and SO_4'' come together. Its solubilit places it at the limit of what can be used in analysis; when necessar therefore, the solubility is reduced by the addition of alcohol.

In order to convert strontium sulphate into other salts, it i reduced to strontium sulphide with charcoal: $SrSO_4 + 4C = SrS +$ $4CO$; this can be easily decomposed with acids. To prepare th hydroxide from it, the sulphide is heated in a current of steam $SrS + 2H_2O = Sr(OH)_2 + H_2S$. By systematic crystallisation fror aqueous solution, also, the sulphide can be decomposed, as in th case of calcium (p. 521), into hydroxide, which crystallises out, an hydrosulphide, which remains in solution; by boiling the solutio sulphuretted hydrogen can be expelled and the separation can thu be continued.

Strontium Nitrate, $Sr(NO_3)_2$, crystallises anhydrous, and i readily soluble in water; it is used in pyrotechnics for making re fire. For this purpose it is mixed with potassium chlorate and a combustible substance, sulphur or charcoal. Strontium has the property of imparting a red colour to flames, and by this means it can be readily detected, as the coloration also appears in the non-luminous gas flame. The spectroscopic decomposition of this dazzling light shows it to be fairly complex; a sharp blue line is the most characteristic.

Barium, Ba, has the combining weight 137·4, and occurs naturally as sulphate and carbonate.

Metallic barium is of a white colour, melts at a red heat, and reacts more energetically with water than strontium or calcium. We have here, therefore, a repetition of the same state of affairs as in the group of alkali metals, viz., the action with oxygen and oxygen compounds is more energetic the higher the combining weight of the metal.

Metallic barium is prepared by the same methods as were given for strontium. It has as yet not found any application whatever.

Barium forms only the divalent ion $Ba^{\cdot\cdot}$, which is colourless and has a poisonous action on the organism. It can be readily detected by means of the exceedingly difficultly soluble precipitate which it yields with sulphanion, SO_4''.

Barium Oxide, BaO, is obtained most readily as a white, heavy, crystalline mass, by the decomposition of the nitrate by heat, nitrogen peroxide and oxygen being evolved and barium oxide remaining behind: $2Ba(NO_3)_2 = 2BaO + 4NO_2 + O_2$. The temperature at which barium carbonate loses its carbon dioxide is so high that it is not suitable for the preparation of the oxide.

The oxide unites with water, with the evolution of much heat, to form barium hydroxide or baryta, $Ba(OH)_2$. This is still more readily soluble in water than strontium hydroxide and, like the latter, it crystallises from its hot saturated solutions in large crystals with $8H_2O$. A solution saturated at room temperature contains 3·7 per cent hydroxide; it is therefore about $\frac{1}{4}$th normal (p. 187) with respect to hydroxyl.

Baryta is used for various purposes. Its dilute solution is used for the volumetric estimation of acids (p. 187); for this purpose it is specially suitable from the fact that it attacks glass much less than a corresponding solution of caustic potash or soda, and because it can never contain carbonate, from the fact that barium carbonate is a very difficultly soluble salt, and is therefore precipitated as soon as it forms. This last circumstance is of importance, because the presence of carbonic acid renders the reactions of alkalimetric indicators indistinct, and therefore impairs the exactness of the determination. To prevent the atmospheric carbon dioxide changing the titre of the solution, the bottle and burette used for baryta are furnished with guard-tubes filled with soda lime, and are always kept connected with one another, as is shown in Fig. 111. The burette is filled by sucking at th indiarubber tube *g* and opening the clip *b*.

* Baryta is also used in analytical chemistry in cases where it i necessary to employ a strong base, the excess of which can be subsequently readily removed. Thus magnesium is separated from potassium and sodium by preparing th sulphates and adding excess of baryt to the solution of these. All thre elements are thereby converted int hydroxides; that of magnesium i precipitated, while those of the othe metals, along with the excess o baryta, remains in solution. If carbo dioxide is now passed into the solution, the barium is precipitated a carbonate, and, after filtration, ther is obtained a solution of the alkal carbonates. The precipitate consist of barium sulphate, barium carbonate, and magnesium hydroxide; it i treated with dilute sulphuric acid, whereby the magnesium hydroxid passes into solution as sulphate, and all the barium is converted into sulphate. The two can be easily separated by filtration.

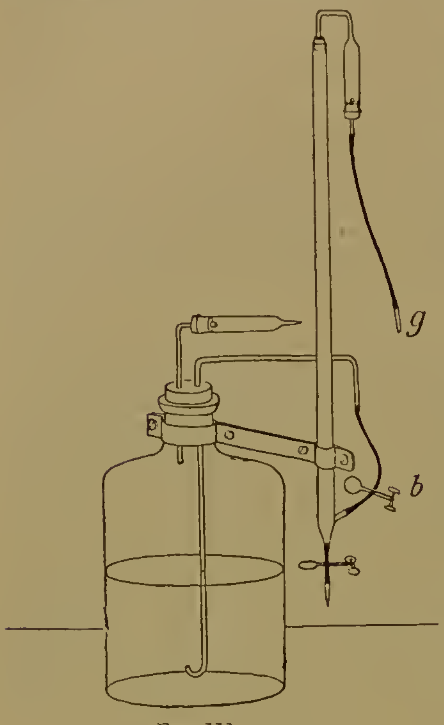

Fig. 111.

For manufacturing purposes also, baryta can be similarly employed. It has already been mentioned that pure caustic potash or caustic soda can be prepared from the sulphates by means of baryta (p. 474).

For the preparation of baryta, barium sulphate is chiefly employed. This is reduced to sulphide by means of charcoal, and converted into hydroxide with steam (cf. the corresponding processes in the case of strontium). From the solution of the sulphide, also, the sulphur can be removed by boiling with a metallic oxide, *e.g.* copper oxide: $BaS + CuO + H_2O = Ba(OH)_2 + CuS$.

Barium Sulphate, $BaSO_4$, occurs fairly widely distributed in nature as the mineral heavy spar or barytes. Both these names are in allusion to the great density which this compound, like all barium compounds, exhibits; it amounts to 4·5, while that of most of the nonmetallic minerals is about 2·5.

Barium sulphate crystallises in rhombic forms, and is isomorphous with anhydrite and celestine. It is formed in all cases where the ions $Ba^{\cdot\cdot}$ and SO_4'' come together, and, as it is very difficultly soluble, it is immediately deposited as a white, heavy precipitate. The use of soluble barium salts, *i.e.* of barion, for the detection and determination of sulphanion, which follows from the above reaction, has already been several times mentioned.

Since sulphuric acid is a strong acid, other acids do not have any great solvent action on barium sulphate. Further, since barium can in no way pass into other more complex ions, there is no solvent whereby barium sulphate can be rendered soluble in aqueous liquids. It can be dissolved only in some substances which do not have an ionising action, *e.g.* concentrated sulphuric acid. So soon, however, as the ions are caused to be formed by dilution with water, the barium sulphate is again precipitated.

On account of this resistance to chemical attack, the naturally occurring heavy spar, when cut in plates, is used in the manufactures for lining apparatus in which strong acids are worked with. The artificially prepared barium sulphate is used as a pigment, under the name "permanent white." It is prepared by dissolving the naturally occurring barium carbonate in hydrochloric acid, and precipitating the clarified liquid with sulphuric acid. Hydrochloric acid is regenerated and can be used for dissolving further quantities of carbonate.

In order to convert barium sulphate into other barium compounds, it is reduced with charcoal to barium sulphide, which can be readily decomposed by acids with evolution of sulphuretted hydrogen. By fusion with excess of alkali carbonate it is converted into barium carbonate; the alkali sulphate which is formed can be removed by washing.

Barium Carbonate, $BaCO_3$, occurs naturally, as *witherite*, in rhombic crystals which are isomorphous with aragonite and strontianite. It is used as a convenient starting material for the manufacture of other barium salts, for which purpose the substance is decomposed by acids. Its conversion into oxide by heating is not practicable, because the temperature of measurable dissociation is too high.

On bringing the ions $Ba^{\cdot\cdot}$ and CO_3'' together, barium carbonate is obtained as a white precipitate, readily soluble in almost all acids.

In preparative chemistry, pure barium carbonate is very largely used for the preparation of the barium salts of the most varied acids. These mostly crystallise well, and can therefore be easily freed from impurities. Their most important property is, however, that they are suited for the preparation of the free acid in aqueous solution, because they are all decomposed by sulphuric acid, barium sulphate being thereby precipitated, and the acid in question remaining free in solution. Examples of this have already been given (*e.g.* p. 213).

Barium Chloride, $BaCl_2$, is obtained by dissolving witherite or barium sulphide (from sulphate and charcoal) in hydrochloric acid; on concentrating the solutions, barium chloride crystallises out in lustrous, heavy crystals with $2H_2O$, which become anhydrous only at a fairly high temperature. Unlike the chlorine compounds of the other metals of this group, barium chloride does not lose hydrochloric acid on dehydration, but maintains its neutral reaction.

Barium chloride is used in the laboratory as a reagent for th detection and estimation of sulphanion.

Barium Nitrate, $Ba(NO_3)_2$, is a salt which is not abundantl soluble in water, and which is employed in analytical chemistry i place of barium chloride, when it is not desired to introduce chloridio into the solution. If free nitric acid is added to a saturated solutio of the salt, a crystalline precipitate of barium nitrate is soon deposited The same occurs when nitric acid is added to the solution of any othe barium salt.

This reaction is not especially peculiar to barium nitrate, but depends on the increase of the nitranion by means of nitric acid and th corresponding overstepping of the solubility product (p. 441); in th case of barium nitrate, however, the phenomenon is specially we marked, because this salt stands at the limit of those which a designated as soluble (100 parts of water dissolve about 9 parts c the salt at 18°), and its solubility product is therefore easily exceede The beginner is sometimes deceived by this precipitate, mistaking i for barium sulphate; the distinctly crystalline nature and the solubility in pure water, after pouring off the mother liquor, are, howeve sufficient to distinguish them.

Barium nitrate is used in pyrotechnics for the preparation of gree fire. The green flame-coloration is produced also in a non-luminou gas flame, especially when the specimen containing barium is moistene with hydrochloric acid. On spectroscopic examination it yields fairly complicated spectrum, which is characterised by a sharp yellow green and a sharp, although less bright, green-blue line, along wit several broad bands.

Barium Peroxide, BaO_2, is obtained as a white powder by heating barium oxide to a temperature between 450° and 550° in a curren of oxygen. At a higher temperature it again loses oxygen, and th equilibrium between the solid oxide and peroxide and the gaseou oxygen, is governed by exactly the same laws as the dissociation o calcium carbonate (p. 512).

Barium peroxide is important as being the most convenient startin substance for the preparation of hydrogen peroxide (p. 153). Fo this purpose it is treated with dilute acid, whereby the reaction occurs $BaO_2 + 2H^{\cdot} = Ba^{\cdot\cdot} + H_2O_2$. The anion of the acid forms the corresponding barium salt, *e.g.* $BaO_2 + 2HCl = BaCl_2 + H_2O_2$.

* It would apparently be most suitable to carry out this reactio with sulphuric acid, because the barium sulphate, being practicall insoluble, would be deposited and leave a pure solution of hydroge peroxide. This, however, cannot be done, since sulphuric acid scarcel attacks the anhydrous barium peroxide. The reaction, howeve readily occurs with hydrochloric acid, and the operation is carried ou

as follows. A certain amount of hydrochloric acid is saturated with peroxide, the barion is precipitated with sulphuric acid, and the solution, which now contains hydrochloric acid, is allowed to act on fresh portions of peroxide. These alternate operations are continued until sufficient hydrogen peroxide has accumulated in the solution. The chloridion is then precipitated by the addition of silver sulphate, and the sulphanion thereby introduced is removed with baryta.

* Another method is to first add a small quantity of baryta water to the hydrochloric acid solution of peroxide in order to remove the metallic oxides present as impurities, and then to precipitate the filtered liquid with baryta. Barium peroxide again separates out; now, however, in the form of a crystalline hydrate, which can be readily decomposed with sulphuric acid. The hydrate is freed from the barium chloride present by washing, and is preserved for use in the moist state, since on being dried it again becomes more difficultly decomposable.

The composition of the hydrate is $BaO_2 . 8H_2O$.

Beryllium.—Beryllium occupies the same position among the alkaline earth metals as lithium does among the alkali metals. Its combining weight is the smallest, and its similarity to the other elements of the group is least. Its properties exhibit a distinct tendency towards the next group, that of the earth metals. The combining weight of beryllium amounts to 9·1.

Metallic beryllium can be prepared by electrolysis, by the reduction of the oxide with magnesium, of the chloride with sodium, and in other ways. It is a white metal, which is still more stable to moist air than magnesium, and decomposes water only slowly even when heated. It is readily dissolved by dilute acids, with evolution of hydrogen, and passes thereby into the ionic state.

Besides the typical divalent ion $Be^{\cdot\cdot}$, beryllium also forms other ions containing oxygen; these will be discussed later. Of the metals hitherto considered, it is the first that is capable of forming different ions.

Beryllion, $Be^{\cdot\cdot}$, is colourless and is distinguished by a conspicuously sweet taste. This fact procured for the element the passing name of glucinum (still occasionally used in France and England); the name beryllium is derived from that of its most important naturally occurring compound, beryl, which is a silicate containing aluminium.

Beryllion forms various salts, of which the chloride, $BeCl_2$, and the sulphate, $BeSO_4$, are the best known. They are both soluble in water, and the solutions react acid. This is due to incipient hydrolysis, since beryllium hydroxide is a weak base.

Beryllium hydroxide, $Be(OH)_2$, is obtained as a white, gelatinous precipitate on bringing beryllion and hydroxidion together; it is not measurably soluble in water, and has no basic reaction. It dissolves in acids, with formation of beryllium salts, and on being heated is converted nto a white powder of beryllium oxide.

Beryllium hydroxide dissolves in caustic potash or caustic sod Since these bases, by reason of their containing hydroxyl, should, i accordance with well-known principles, diminish the solubility of bery lium hydroxide, this contradiction requires an explanation. This yielded by the fact that the compound BeO_2H_2 can split off hydrio and behave like a very weak acid. Accordingly, it gives the two ion $HBeO_2'$ and BeO_2'' (just as carbonic acid gives the ions HCO_3' an CO_3''), and it is these and not beryllion, $Be^{\cdot\cdot}$, that are present in th solution in question. The compound is also obtained by fusing bery lium hydroxide with caustic soda and dissolving the melt in water.

If this alkaline solution is allowed to stand a long time, or if it heated to boiling, almost all the beryllium hydroxide is precipitate The question now arises why the chemical equilibrium, which had pr viously existed, is now disturbed, since no new substance has bee added. The answer is to the effect that the beryllium hydroxid which is precipitated is a different, and indeed a more stable an less soluble, form of the hydroxide than the freshly precipitated for which is soluble in alkalis. In other words, the newly prepared sol tion is supersaturated with respect to the more stable form of th hydroxide, and therefore cannot continue to exist when the latter for is present. Since this form is not present in the newly prepare solution, the precipitation can commence only after the first traces it have been formed. At the ordinary temperature this occurs slowl but quickly when heated.

Summary.—The properties of the corresponding compounds the elements of the second group change in the same order as the con bining weights, so that the relations which here prevail can be easil impressed on the memory by making the sense clear in which th change takes place. In the following table the properties which hav been considered are given, and the arrows which are added indicat whether the values of these increase (→) or decrease (←) with increa ing combining weight.

PROPERTIES OF THE ALKALINE EARTH METALS AND OF THEIR COMPOUNDS

Combining weight	→
Reactivity of the metal	→
Density of the elements and of the corresponding compounds	→
Basic properties of the hydroxides	→
Solubility of the hydroxides	→
Solubility of the halogen compounds and nitrates	←
Solubility of the sulphates	←

CHAPTER XXVI

ALUMINIUM AND THE OTHER EARTH METALS

General.—The group of the earth metals, to which we now turn, is characterised by the fact that the elements contained in it form trivalent ions. The parallelism which exists between the elements of the first and second groups in respect of combining weights and general character, is also found here, with, however, an essential difference. Of the elements of the third group, there is only one which occurs frequently in the earth's crust; but this one is found n great abundance. All the other elements are exceedingly rare, and their properties and compounds are therefore comparatively little known.

The diminution of the reactivity of the metal with oxygen and water, which was met with in some of the members of the second roup, is found here in a still higher degree, so that aluminium, the most important element of the third group, is a metal which is at the resent day applied in the arts, and as such plays a not inconsiderable ôle. At the same time, the basic properties of the hydroxides, a eakening of which was also indicated in the second group, have ecome so small that there is no strong base in this group. As usual, is in the case of the elements with *small* combining weight that this fect is most conspicuous; in the case of the first element which must e included in this group, viz., boron, the complete reversal has already ken place, for this element has entirely lost its metallic character nd forms an acid hydroxide, boric acid (p. 429).

The elements belonging to this group, together with their combin- g weights, are :—

Boron (11·0), aluminium (27·1), scandium (44·1), yttrium (89), nthanum, etc. (138), ytterbium (173). With regard to these we ould make the following remarks.

While the combining weights from boron to lanthanum correspond those of the metals lithium to cæsium and beryllium to barium, e have here a higher member, ytterbium, with a combining weight 3, which is not represented in the first two groups. It may be presumed that such representatives do exist, but have not yet bee discovered.

Further, an etc. has been inserted after lanthanum. This signifi that there exist at this point not one element but a number of elemen which are all very close to one another, and have therefore an almo equal claim to this position. This occurrence of several elements wit small differences recalls the occurrence of numerous small planeta bodies at a part of the solar system where, by analogy, one woul have expected a large planet.

Aluminium.—Of all the light metals, aluminium is the mo widely distributed on the earth's surface. It forms a constituent almost all crystalline silicate rocks; and of the secondary formation the clays and slate formations are formed from aluminium silicate. knowledge of the compounds of this metal, therefore, extends back far as chemical knowledge at all can be traced.

From the time of the discovery of the alkali metals, it was regard as indubitable that a metal must be contained in clay. Wöhler, ho ever, was the first to obtain metallic aluminium by the action sodium on the chloride. The method of separating the element fro its compounds by electrolysis was given by Bunsen (1854).

The name aluminium is derived from alum (alumen), becau aluminium is contained in this long-known salt.

At the present day, aluminium is prepared on a very large sca by the electrolysis of its oxide. The oxide is fused by the he developed by the passage of the electric current, the aluminium go to the cathode, and the oxygen which separates at the anode combin with the charcoal, of which the anode consists, to form carbon mo oxide. To facilitate the fusion, the electrolytic vessel also contai other compounds of aluminium, *e.g.* cryolite (*vide infra*); since oxyg is more readily separated than fluorine (which is the correspondi other constituent of cryolite), this addition does not alter the chemi reaction, and only aluminium oxide requires to be thrown in to repla the used up material.

Metallic aluminium is a white, somewhat bluish metal whi remains tolerably unchanged in the air. This is due to the fact th it quickly becomes covered with an invisible, thin, and firmly adheri layer of aluminium oxide, which protects the metal underneath like varnish. It melts at 700°, and can be both cast and mechanical wrought into the shape desired, as it is not hard and is very ducti Thus, thin wire and very thin foil, like gold-leaf and silver-leaf, c be made; the latter is greatly used for "silvering," since sulphuro gases do not blacken it. Aluminium is a good conductor for heat a electricity.

On account of its lightness (density = 2·7), its silver-like lustre, a its durability in the air, aluminium, especially since the electroly method has rendered it cheap, has become greatly used for ordina utensils, but it does not seem hitherto to have been received with entire favour. This is perhaps to be accounted for by the fact that although it resists the action of pure water, it is rather strongly attacked by salt solutions of all kinds. Further, the oxidation of the metal generally occurs in spots, so that holes are there formed which can be repaired only with difficulty.

* When aluminium is alloyed with mercury, it appears to assume quite different properties. It is amalgamated by rubbing its surface with a mercury salt, *e.g.* mercuric chloride, with some pressure. The parts which were at first bright on account of the mercury, immediately become dull, and a moss-like growth of aluminium hydroxide arises from them, the aluminium undergoing oxidation. This phenomenon is explained by the fact that, although the protecting layer of oxide is formed at the amalgamated parts, the coating does not adhere, on account of the liquid nature of these, and the oxidation, therefore, pursues its course. It is not that the mercury produces an increased reactivity of the aluminium (a thing which is theoretically impossible), but the real chemical activity of the aluminium is allowed free scope to exert itself.

* The amalgamated aluminium is employed as a reducing agent. On account of this behaviour, objects made of aluminium must be carefully protected from contact with mercury.

While, even at comparatively high temperatures, massive aluminium is only superficially and inappreciably attacked by oxygen, the finely divided metal burns with a brilliant light at a red heat. This can be shown by holding aluminium foil in the flame, or by blowing finely divided metal, such as is used in the form of aluminium bronze, through the flame. It takes fire, however, with greater difficulty than magnesium.

Aluminium dissolves in dilute hydrochloric and sulphuric acids with energetic evolution of hydrogen. In nitric acid it readily becomes passive, *i.e.* becomes coated with a layer which is not attacked by the acid, and then remains unchanged. Further, aluminium readily dissolves in a solution of caustic potash or soda, with evolution of hydrogen. This is due to the formation from the aluminium of an anion containing oxygen; we shall return to this later (*vide infra*). Salt solutions, also, especially solutions of ammonium salts, dissolve the metal fairly readily.

Aluminium forms alloys with various metals, and some of these are technically valuable. They will be mentioned under the respective metals. We would only mention here that an alloy (magnalium) has been prepared from aluminium and magnesium, which is stated to have technically valuable properties, and to be stable in the air.

Aluminion.—Aluminium forms a single, elementary, trivalent ion, $Al^{\cdot\cdot\cdot}$; it can further act as a constituent of complex ions.

Aluminion is colourless, and its salts are for the most part soluble.

They have an astringent taste, but have otherwise no great physi logical action. Since aluminium hydroxide is a weak base, all th salts of aluminium are hydrolytically dissociated to an appreciabl extent in aqueous solution, and therefore react acid. In the case the salts of the strong acids, this hydrolysis is slight; in the case the salts of weak acids, however, it becomes considerable, especially o heating.

Unlike the ions of the other more frequently occurring ligh metals, aluminion does not occur in measurable amount in natur waters. It is separated out from the rocks in the form of aluminiu silicate, an exceedingly difficultly soluble compound, and in this for (p. 422) it is widely distributed in nature.

Aluminium Hydroxide.—Aluminium hydroxide, $Al(OH)_3$, i precipitated as a gelatinous, uncoloured precipitate from solutions aluminium salts, by the addition of a soluble base; in the air it lose water, and when heated to redness is converted into aluminium oxid according to the equation $2Al(OH)_3 = Al_2O_3 + 3H_2O$.

Aluminium hydroxide is practically insoluble in water, and is very weak base. Since it contains three hydroxyls, it can form thre kinds of salts, in which one, two, or three hydroxyls are replaced b anions. Salts in which unreplaced hydroxyl is still present are calle basic salts, corresponding to the acid salts which contain unreplace acid hydrogen. In general, however, the basic salts are much les definitely characterised than the acid ones; whereas the latter mostl crystallise well, and can therefore be easily prepared in the pure stat the amorphous form predominates in the case of the basic salts, whos preparation in the pure state is therefore difficult. For this reaso they will, in the sequel, generally not receive special description.

On account of the slight development of basic properties in th case of aluminium hydroxide, and its exceedingly small solubility, it i precipitated even by very weak soluble bases, *e.g.* by ammonia, even i presence of ammonium salts. In this way it differs from the hydrox ides of the alkaline earth metals, and can, therefore, be used for th separation of aluminium from these, especially from magnesium.

Caustic potash or soda of course also precipitate aluminium hydrox ide from the solutions of its salts. The hydroxide, however, readil redissolves in an excess of these substances, and forms clear solution of a strongly alkaline reaction. This is due to the fact that aluminiu hydroxide can also act as an acid by splitting off hydrion from it hydroxyl groups (*vide infra*).

This property of aluminium hydroxide of acting as an acid, is th cause that metallic aluminium readily dissolves in caustic potash o soda with evolution of hydrogen (p. 549). If such a solution and als one of aluminium in hydrochloric acid are prepared, and the two solu tions are mixed, aluminium hydroxide is precipitated, and sodiu chloride remains in solution. The reaction is represented by th equation $Na_3AlO_3 + AlCl_3 + 3H_2O = 3NaCl + 2Al(OH)_3$. Taking the reacting ions into account, we should write, $AlO_3''' + Al^{\cdot\cdot\cdot} + 3H_2O = 2Al(OH)_3$.

By loss of water, aluminium hydroxide can give rise to various anhydrides, which bear the same relation to one another as the anhydrides of phosphoric acid. According as one, two, or three combining weights of water are eliminated from two combining weights of the hydroxide, there are obtained, besides $Al(OH)_3$, the compounds $Al_2O_5H_4$, AlO_2H, and Al_2O_3.

All these compounds occur in nature: the normal hydroxide $Al(OH)_3$ is hydrargillite; $Al_2O_5H_4$ (generally greatly contaminated with other substances) is bauxite; AlO_2H is diaspore; and Al_2O_3 is corundum.

Bauxite is of importance as being the starting substance in the manufacture of metallic aluminium (p. 548). Corundum is, on account of its hardness, which is nearly equal to that of diamond, an important mineral technically. It crystallises in rhombohedra. In its fine-grained varieties, called emery, it is employed as a grinding material for glass, steel, and other hard substances. Transparent corundum, coloured blue by admixtures, is valued as a gem under the name sapphire; a red form, whose colour is due to a small amount of chromium, is called ruby, and is also a valuable gem. Small and less finely coloured rubies are used as axle-bearings in watches and other measuring instruments, where movement with as little friction as possible is required. Corundum, in all its forms, is very little susceptible to chemical influences, and it is only with difficulty that it can be brought into soluble forms by fusion with caustic alkalis or acid sulphates.

Aluminates.—The compounds in which aluminium hydroxide occurs as an acid, are called aluminates. Since aluminium hydroxide contains three combining weights of hydrogen, it must be regarded as a tribasic acid; since, however, it is a very weak acid, the normal compounds, in which all three hydrogens are replaced, are not easy to prepare, and in aqueous solution they decompose to a greater or less extent owing to hydrolysis.

* A substance which is capable of acting at the same time as acid and as base, can be only a *weak* acid and base. For the acid action necessitates the presence of hydrion; the basic action, that of hydroxidion. The two kinds of ion, however, cannot be present together in any great concentration, since they would unite to form water, which is only very slightly dissociated. If, therefore, an acid is strong, *i.e.* splits off much hydrion, it certainly cannot split off more than an exceedingly small amount of hydroxidion, the amount of which is limited by the chemical equilibrium of the two ions in water. The same holds for weak bases.

As in the case of phosphoric acid, the aqueous solutions of the aluminates contain three different anions, viz., the monovalent H_2AlO_3', the divalent $HAlO_3''$, and the trivalent AlO_3'''. Since we are dealing with a weak acid, the monovalent ion will predominate.

Of the aluminates, the sodium compounds, more especially, are known; they correspond to the three possible types, NaH_2AlO_3, Na_2HAlO_3, and Na_3AlO_3. These substances are soluble in water, and do not crystallise well; their solutions react strongly alkaline, and are very unstable. For if such solutions, especially of the first and second types, be kept some time, they lose a great part of the alumina they contain, this being deposited as a crystalline precipitate on the bottom of the vessel. This is due to the same phenomenon as in the case of beryllium hydroxide (p. 546); the aluminium hydroxide which is deposited is a more stable form than the amorphous and gelatinous one, and solutions, therefore, which are saturated with respect of the latter are supersaturated with respect of the former. Accordingly, so soon as the first crystals of the more stable form are produced, it continues to separate out, and does not stop until the new equilibrium is reached.

Aluminium hydroxide is not soluble in ammonia, because the basic properties of the latter are too weak. That is to say, if ammonion and aluminanion are brought together, they pass into the undissociated compounds, ammonia and aluminium hydroxide, as is shown by the equation $H_2AlO_3' + NH_4^{\cdot} = Al(OH)_3 + NH_3$. This behaviour is made use of in analysis. When it is required to precipitate aluminium hydroxide from an aluminate, an acid may be used for the purpose; an excess of the acid, however, again dissolves the alumina, and it is therefore difficult to effect a complete separation. If, however, an ammonium salt be added to the solution of an aluminate, the above reaction takes place and the alumina is deposited, while an excess of ammonium salt exerts no solvent action.

The other light metals also form aluminates. Of these, the naturally occurring *spinel* is of interest; this can be regarded as the anhydride of monomagnesium aluminate, $MgH_4Al_2O_6$, for it has the composition $MgAl_2O_4$, and $MgH_4Al_2O_6 - 2H_2O = MgAl_2O_4$.

Spinel crystallises in the regular system, generally in rhombic dodecahedra, and is the type of a fairly large series of corresponding isomorphous compounds which are composed of equal combining weights of the oxides of a divalent and a trivalent metal, for the formula of spinel can also be written $MgO + Al_2O_3$.

Since the place of magnesium can be taken by iron, manganese, zinc, etc., and that of aluminium by chromium, iron, manganese, etc., there are a large number of compounds of the type of spinel, some of which will be mentioned later.

Aluminium Chloride.—The compound $AlCl_3$ is formed when metallic aluminium is heated in a current of hydrogen chloride. Hydrogen is liberated, and aluminium chloride readily sublimes, forming a white crystalline mass in the colder parts of the apparatus.

Formerly, when aluminium was not a cheap substance, the chloride was prepared by heating a mixture of aluminium oxide and charcoal in a current of chlorine. The process is represented by the equation $Al_2O_3 + 3Cl_2 + 3C = 2AlCl_3 + 3CO$.

Aluminium chloride boils at about 183°. The melting point is somewhat higher, 193°; on being heated, therefore, under ordinary pressure, it passes directly from the solid into the vaporous state. By heating it in a closed vessel, so that the boiling point is raised, it can be fused.

* Aluminium chloride is used in organic chemistry in numerous preparations, which depend on the fact that in presence of aluminium chloride mixtures of a chlorine and a hydrogen compound split off hydrogen chloride, the residues then combining to form the new compound. In organic chemistry such a process is called synthesis (in the narrower sense), and for such purposes aluminium chloride is of especial importance.

Aluminium chloride fumes in the air and reacts with water with a very considerable evolution of heat. Anhydrous aluminium chloride cannot be again obtained from the aqueous solution; from the strongly concentrated solution a salt crystallises out with $2H_2O$, which, on being heated, completely decomposes into hydrogen chloride which escapes, and aluminium oxide which remains behind: $2AlCl_3 + 3H_2O = Al_2O_3 + 6HCl$.

Aluminium chloride readily unites with other chlorides to form double salts, and more especially so with potassium and sodium chlorides. These compounds crystallise well, and in them aluminium chloride has lost its volatility. The sodium compound melts with exceeding ease, and was formerly used as the starting substance for the preparation of metallic aluminium.

On account of its ready volatility, the molar weight of aluminium chloride was early determined, and was found, in agreement with certain theoretical assumptions, to correspond to the formula Al_2Cl_6. Subsequently, these theoretical views became doubtful, and a thorough investigation showed that in the neighbourhood of the boiling point, certainly, vapour densities were observed which corresponded approximately to this formula (although they were always too low), but that the values rapidly diminished as the temperature rose, and at temperatures between 450° and 760° remained constant and corresponded to the formula $AlCl_3$.

Aluminium Bromide and Aluminium Iodide are very similar to the chloride, but less volatile. They are readily formed from the elements, and in organic chemistry have a use similar to that of the chloride.

Aluminium Fluoride, AlF_3, is obtained at a red-heat from aluminium and hydrogen fluoride, and also from aluminium oxide and hydrogen fluoride, and is very much less volatile than the other halogen compounds of aluminium. It forms small, lustrous crystals which behave indifferently towards water, and scarcely dissolve in it. If alumina is treated with aqueous hydrofluoric acid, it dissolves in fair quantity. The solution, however, is strongly supersaturated with respect to the above difficultly soluble form of aluminium fluoride, which is slowly deposited spontaneously.

Aluminium fluoride is soluble in hydrofluoric acid, and forms with it hydrofluoaluminic acid, H_3AlF_6, the sodium salt of which is very difficultly soluble in water. It occurs in large quantities in Greenland, and as a mineral this compound, Na_3AlF_6, is called *cryolite.*

Cryolite is used for the preparation of soda along with pure aluminium hydroxide. For this purpose it is heated with milk of lime or fused with lime, whereby calcium fluoride and sodium aluminate are formed; the latter passes into solution or can be extracted with water: $Na_3AlF_6 + 3CaO = 3CaF_2 + Na_3AlO_3$. The aqueous solution is decomposed by passing in a current of carbon dioxide, whereby sodium carbonate is formed and aluminium hydroxide is precipitated: $2Na_3AlO_3 + 3CO_2 + 3H_2O = 3Na_2CO_3 + 2Al(OH)_3$.

Aluminium Sulphate.—Of all the salts of aluminium, the sulphate is the one which has the largest application, and it is therefore manufactured on a large scale. It is obtained by heating aluminium hydroxide with sulphuric acid; the solution produced solidifies, at a suitable concentration, to an indistinctly crystalline mass of the formula $Al_2(SO_4)_3 + 18H_2O$. The sulphate can also be prepared by heating aluminium silicate with sulphuric acid, silicic acid being thereby set free. A pure salt can be obtained from the commercial product by precipitating the concentrated solution with alcohol. An oily liquid is then deposited, which is a supersaturated solution of aluminium sulphate in water (with a very little alcohol); this soon solidifies to lustrous scales of a salt with $18H_2O$.

* It is no rare thing for aqueous solutions of salts which are difficultly soluble in alcohol, to be first precipitated, by the addition of the latter, as a concentrated solution which is immiscible with the rest of the alcoholic solution. The formation of the supersaturated solution before that of the solid crystals is only another case of the prior occurrence of the less stable forms.

On account of hydrolysis, the aqueous solution of aluminium sulphate reacts acid. It can dissolve fairly considerable quantities of aluminium hydroxide, with formation of basic salts; difficultly soluble basic salts are ultimately deposited.

A basic aluminium sulphate, in which only one of the three hydroxyls is replaced by sulphanion, $Al_2(OH)_4SO_4 + 7H_2O$, occurs naturally as aluminite, and is used in the preparation of the normal aluminium sulphate, and of its double salt, alum.

Alum was the name given originally to a double salt of aluminium and potassium sulphate, $AlK(SO_4)_2 \cdot 12H_2O$, which crystallises in fine octahedra belonging to the regular system, on mixing the solutions of the single salts. In the cold it is much less soluble than the single salts, and a solution prepared from the saturated solutions of these is strongly supersaturated in respect of alum. The supersaturation does not, it is true, disappear spontaneously, as the solution is in the metastable condition; in our surroundings, however, solid alum is so largely distributed that scarcely an object which has lain in the air is free from it. As a rule, therefore, the nucleus which is necessary for the formation of crystals is immediately present. If this is excluded by heating the liquids and vessels to 100° (whereby the alum melts in its water of crystallisation) and the entrance of dust avoided, crystallisation remains suspended for any length of time.

Alum was formerly the most important salt of aluminium. Although the potassium sulphate contained in it had either no effect or had a disturbing effect in its applications, alum was nevertheless employed, because none of the simple salts of aluminium crystallise well, and thus cannot be easily freed from impurities. Since the method was discovered of preparing pure aluminium hydroxide (by way of sodium aluminate), and so of preparing pure aluminium sulphate from this, alum has lost its importance, and is now being more and more replaced by the simple sulphate.

* With this also, the former methods of preparing alum are beginning to disappear. It used to be prepared from a basic potassium aluminium sulphate, which occurs naturally as alum-stone, by heating this and extracting with water; alum thereby passed into solution and aluminium hydroxide remained behind. Further, it was obtained from alum shale, a silicate of aluminium permeated with sulphide of iron. This was roasted, and then allowed to undergo oxidation in the air. From the sulphur of the iron sulphide, sulphuric acid is formed; this converts the aluminium silicate into sulphate, which is then extracted with water and made to crystallise by the addition of potassium sulphate.

On being heated, alum melts in its water of crystallisation; on raising the temperature, it loses its water and forms a spongy, white mass called *burnt alum*. The latter is used in medicine.

The most important use of aluminium sulphate, or of alum, is in dyeing. Many dyes are incapable of combining directly with the fibre of the cloth in such a way that the colour is not withdrawn by water and soap. If, however, the cloth is previously treated with aluminium salts it can be permanently dyed. This is due to the fact that the fibre absorbs and unites with the aluminium hydroxide, which is always present in the solution, as the aluminium salts are always somewhat hydrolysed. Further, the dyes have the power of uniting with aluminium hydroxide to form the practically insoluble, finely-coloured "lakes," and in this way the union between the dye and the fibre is effected by the aluminium hydroxide.

Potassium aluminium sulphate is the type of a large series of double salts, which have a similar composition, and crystallise in the same forms of the regular system. The place of potassium can be taken by rubidium, cæsium, ammonium, and a large number of organic derivatives of ammonium, as well as by the heavy metal thallium, but not by sodium or lithium. The place of aluminium can be taken by other metals, which form trivalent ions, such as iron, chromium, manganese, indium, etc. Finally, in place of the sulphanion we can have selenanion, SeO_4''. Hence, we have a great diversity here; for all these double salts the name alum has been adopted, the names of the metals present being prefixed. These alums are isomorphous with one another, and the supersaturated solution of one of them is made to crystallise by a nucleus of any other.

Aluminium Silicate.—It has already been several times mentioned that the rocks of which the earth's crust was primarily formed consist essentially of silicates, the metals of which, besides the frequent alkali and alkaline earth metals, formerly mentioned, are aluminium and iron. On undergoing decomposition by water and carbon dioxide ("weathering"), the first mentioned pass into carbonates, while magnesium partially, and aluminium entirely, remain behind as simple silicates.

Aluminium silicate is called *clay*, and is formed in the amorphous state, and in very finely divided form, in the weathering of the rocks. As a result, it is readily carried away by flowing water, and is deposited only when the movement of the water becomes very slow. According to its degree of purity, it possesses various properties, and is called by different names.

The purest form is called *kaolin*, or *china clay*, and is generally found in localities where rocks, poor in magnesium, are decomposed by water and carbon dioxide, but are not transported mechanically. The water has then carried away the other constituents in solution, and the aluminium silicate, with more or less quartz, has remained behind.

Less pure forms, which are frequently contaminated, more especially with calcium carbonate, quartz, and iron oxide, are called *clay*, or *potter's earth*. *Marl* contains a large quantity of calcium carbonate, and *loam* contains quartz sand as well.

The use of aluminium silicate is very old, and widely extended. It depends on the fact that it yields a tenacious mass with water, capable of being moulded; on drying, this undergoes regular contraction, and preserves its form, and on being strongly heated (fired) passes into a stone-like mass, which is not, like clay which has simply been dried, again converted into a plastic form by water, but permanently retains its character. On firing, the clay shrinks still further, and this all the more the more strongly it is heated.

Pure aluminium silicate is very difficultly fusible. The presence of iron or of lime greatly depresses the melting point.

* The various applications of aluminium silicate follow from what has been said above. The least pure form, potter's earth or ferruginous clay, is used for bricks or for vessels of little value, which are moulded, dried, and fired at a low temperature. The fired clay is not impervious to water, as it is permeated by innumerable pores; to render it impervious it is coated with a *glaze*. This is, in general, of the composition of glass (p. 526). Care must be taken that the thermal expansion of the glaze agrees as far as possible with that of the ground material, since otherwise the coating would crack on change of temperature. In the case of cheap earthenware generally, no regard is paid to this, and the latter therefore soon loses its imperviousness with use.

Faience is ware made of white, *i.e.* non-ferruginous, clay, and is coated with white or a coloured glaze; it also is generally not very resistant.

Stoneware is the name given to ware made of difficultly fusible clay. It is glazed by firing it at a high temperature, and throwing common salt into the oven while at its highest temperature. The latter volatilises, and the sodium forms a glaze with the aluminium silicate; this passes continuously into the mass, is thinly and evenly distributed, and is therefore much more resistant than the glaze of faience, which is only brushed on. Vessels of stoneware are used where greater resistance to chemical influences are required, *e.g.* in chemical works.

Finally, the most resistant and the finest material is *porcelain*. This is prepared from the purest aluminium silicate, with the addition of quartz and felspar (*vide infra*); the latter is a double silicate of aluminium and potassium. The ware is moulded and subjected to a preliminary firing at a gentle heat. This "biscuit ware" is introduced into a milk of finely powdered felspar and water; the water is absorbed, and the ware becomes covered with a thin, regular coating of powdered felspar. After being dried, it is heated to a white heat; the felspar thereby fuses, and in the liquid state permeates the clay in all directions. In this way, the union between glaze and support is very complete, so that vessels of porcelain can withstand fairly rapid changes of temperature without breaking and without becoming cracked on the surface.

Double Silicates of Aluminium occur in large numbers in nature. Among the most important may be mentioned the felspars, of which there are various kinds, according to the second metal contained in them. Ordinary felspar, or orthoclase, is potassium aluminium silicate, $AlKSi_3O_8$. It occurs widely distributed in monoclinic crystals, and must be regarded as one of the most important sources of potash in the soil. The soda felspar, or albite, has a corresponding composition, containing sodium in place of potassium; it is triclinic. Anorthite is a calcium felspar, which is isomorphous with albite, and can unite with it in all proportions to form mixed crystals; it has the composition $Al_2CaSi_2O_8$. Some of these mixtures have received special names, such as oligoclase and labradorite.

Another group of alkali aluminium silicates is that of *mica*, which is distinguished by its power of cleaving, its elasticity, and resistance to high temperature. Some kinds of mica contain magnesium in place of the alkali metals. The formula is doubtful.

Other Salts of Aluminium.—Since in using aluminium sulphate as a mordant in dyeing, the alumina is deposited on the fibre, the corresponding amount of acid remains in the solution, and as it increases it begins to hinder the deposition. By using a weak and volatile acid, the process can be carried on to much greater advantage; for such purposes, therefore, *aluminium acetate* is used. This salt is obtained from aluminium sulphate by decomposing it with barium or lead acetate, whereby the corresponding sulphate, being insoluble, is deposited. The same object is attained more simply by the addition of any soluble acetate, *e.g.* sodium acetate, since this has the same effect in diminishing the concentration of hydrion.

Aluminium acetate is a very decomposable salt; even on boiling its aqueous solution it is decomposed into alumina (or a very basic acetate), which is precipitated, and acetic acid, which remains in solution. This is due to the increase of hydrolysis with rising temperature. For, since the hydrolysis depends on the amount of hydrion and hydroxidion contained in the water, and since this increases with rising temperature, because the dissociation of water into its ions is accompanied by absorption of heat, the degree of hydrolysis must also increase as the temperature rises. Moreover, the reaction is thereby accelerated, and long-persisting supersaturation therefore excluded.

Aluminium Phosphate occurs as a mineral in various forms. It is best known as turquoise, which is used as a gem, and is coloured blue, owing to the presence of copper.

Ultramarine is the name given to a substance of a fine blue colour which was first obtained from the *lapis lazuli*, in which it occurs mixed with a colourless matrix, and has been used as a valuable pigment. From analysis, aluminium, silicon, sodium, and sulphur are found to be the chief constituents, and in 1828 Gmelin succeeded in preparing a blue dye-stuff of the nature of ultramarine by treating alumina with Glauber's salt, silicic acid, and charcoal. Since then, the commercial preparation of this colour, which is distinguished by its unchangeableness in light and by its beauty, has grown to a large industry. Kaolin is heated with Glauber's salt, or soda, charcoal, and sulphur, at first with exclusion of air, and the dull-green coloured product is then roasted with sulphur, with access of air, whereupon the blue colour develops. A series of different colours, from red-violet to blue-green, is obtained by varying the relative amounts of the original substances and the method of treatment. The ultramarine is made ready for use by washing with water and levigation.

While ultramarine is stable to light and air, even in the presence of lime, it is decomposed even by weak acids, thereby becoming colourless and evolving sulphuretted hydrogen.

In spite of its having long been known, and of the technical preparation of ultramarine having been practised for many years, the chemical nature of this substance is not yet clear. The sodium in it can be replaced by silver and potassium; so far it behaves like a salt. Its formula, however, is not known, since we have as yet no means of separating the pure substance from any impurities it contains.

* **The other Earth Metals.**—The elements already mentioned which are allied to aluminium, viz., scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, and ytterbium, along with a number of still less certain companions, are all of them very rare, and occur only in isolated parts of the earth's crust, in Scandinavia and in North and South America. Their properties are similar to those of aluminium, subject to the same deviations as were found in the other groups, with increase of the combining weights; that is, the free metals are all the more readily oxidisable the greater their combining weight, and, in the same sense, the bases become stronger.

The hydroxides are white, amorphous precipitates, which, however, no longer dissolve in alkali hydroxides; the higher members are even able to form carbonates. With potassium sulphate they form double salts, which are slightly soluble in water, and almost insoluble in excess of potassium sulphate solution. The latter behaviour is due to the diminution of the solubility by the presence of the sulphanion (p. 441), and is by no means a peculiar property of these double salts. The composition of the double salts, however, does not correspond to that of alum, but is expressed by the formula $MK_3(SO_4)_3$. Further, in the higher members the property of forming more highly oxidised compounds or peroxides is found.

By reason of this close agreement in the properties, it is no easy matter to separate these elements, which generally occur mixed in nature, from one another. Nor are there any methods of separation applicable to them such as are employed for other analytical purposes, but one has to be content with partial separation on the basis of slight differences in solubility, of chemical equilibrium, and of decomposability, by repeated performance of which the object is more or less attained. In fact, almost every investigation which has been carried out with comparative thoroughness has shown that one or other of the substances hitherto regarded as simple is a mixture, and the whole history of the development of this part of chemistry may be designated as the gradual isolation of new individuals from the total amount. It is by no means probable that these separations have already reached a definite conclusion.

As characteristic of the various elements of this group, there is, first of all, the combining weight. By some method or other, a partial separation of the mixture of substances is effected, *e.g.* by partia precipitation of the salt solution with insufficient ammonia, and thi method is repeated until the combining weight of the fractions obtaine no longer changes on further separation. Another very importan criterion is afforded by the optical properties. Many of these element give a very complicated spectrum on allowing the electric spark to pas between carbon points moisted with solutions of their salts. Since under given conditions, each element possesses a perfectly definit spectrum, it can be seen whether the spectrum changes by partia separations. Where this is the case, we are certainly dealing with mixture. The higher members also exhibit absorption spectra, som of them also emission spectra. The former are obtained by allowin white light to pass through solutions of the salt in question, and the examining it with the spectroscope. Dark bands are then seen i definite positions, which are also characteristic for the different elements Further, the oxides of the higher members, when heated to incandescence, do not emit continuous light, as solid substances usually do but the emitted light is found by the spectroscope to consist of isolate bands similar to the light of incandescent gases. In this case, however they are much broader than in the latter case.

Another kind of optical phenomenon, the importance of which fo the characterisation of the elements has not yet been fully demonstrated, consists in the phosphorescence produced by the cathode rays When electrical discharges of high potential are allowed to pas through a highly vacuous space, rays of a special kind are emitted from the cathode, which are propagated in straight lines, and which rende luminous many substances with which they come into contact. The light thus produced differs also in different substances; still, differences occur in cases where chemical differences are unknown, so that it does not appear safe to draw conclusions from the one as to the other.

Scandium, *yttrium*, and *lanthanum* yield colourless salts, and form only one oxide, of the composition M_2O_3. Besides the hydroxide $Ce(OH)_3$, whose salts are colourless, *cerium* yields another hydroxide, $Ce(OH)_4$ (and a corresponding oxide, CeO_2), which also forms salts, whose solutions are brown. We have here, therefore, two kinds of ions whose chemical composition is not different, but which have different properties, depending on the different valency. The trivalent ion, $Ce^{\cdot\cdot\cdot}$, is called tricerion, the quadrivalent ion, $Ce^{\cdot\cdot\cdot\cdot}$, tetracerion, and the corresponding salts are called cerous and ceric salts. The former are converted into the latter by means of oxidising agents; the reverse change is effected by reducing agents. These very important relations will be presently more closely studied in the better known example of iron.

Recently, cerium has become of technical importance from the fact that it is added to thoria, of which the mantles for the incandescent light are made. In the section treating of thorium further particulars of this will be given.

Praseodymium and *neodymium* are characterised by the absorption spectra of their salts. They also form higher oxides, but much less easily than cerium.

CHAPTER XXVII

IRON

General.—Metallic iron was not obtained from its naturally occurrin compounds at so early a date as some of the other metals, especiall copper and tin. This is due to its high point of fusion, and to th much greater difficulty in obtaining it in the metallic state from it compounds. Thus, in prehistoric times iron does not appear unti *after* bronze, *i.e.* mixtures containing copper as essential constituent and was apparently at first a great rarity

Notwithstanding the wide distribution of iron, it scarcely ever occur in the metallic state on account of its tendency to form compound with oxygen and sulphur. The chief occurrence of metallic iron except in some rather accidental cases through the action of chemica processes connected with volcanic activity, is in certain *meteorites* These are masses which do not originally belong to the earth, bu which, in the course of their flight through space, approach so closely to the earth that, owing to atmospheric friction, they lose their kineti energy, which is thereby converted into heat, and fall to the earth Many of these masses consist of iron.

Masses of native iron also occur, although rarely (*e.g.* at Ofvivak in Greenland), whose meteoric origin is doubtful, although no explanation has been given of any other possible origin.

Metallic iron is a grey, tenacious metal, which fuses with grea difficulty, at about 1600°; it combines with free oxygen quickly at high temperatures, slowly at low ones. In the heat essentially compounds of the formula Fe_3O_4 to Fe_2O_3 are formed; in the cold, iron hydroxide, $Fe(OH)_3$, is formed. The hydrogen necessary for this is taken up in the form of water; in fact, iron "rusts" or oxidises at a low temperature only in moist, not, or not measurably, in dry air. Since the rust does not cohere, it does not protect the iron against further oxidation (p. 548).

At all temperatures water is decomposed by iron. The decomposition of water by red-hot iron is a classical experiment (p. 82). Even at the ordinary temperature decomposition takes place with evolution of hydrogen, but exceedingly slowly, so that the evolution of hydrogen can be observed only by using large surfaces (iron powder). Iron is dissolved even by the weakest acids, thereby passing into divalent diferrion with evolution of hydrogen.

The combining weight of iron has been found to be Fe = 56·0.

Commercial Iron.—Commercial iron is not pure, but contains up to as much as 2 per cent of carbon, which has a very great influence on its properties, and also smaller quantities of other impurities. While pure iron, although very tenacious, is comparatively soft, its hardness increases with the amount of carbon it contains, and its behaviour at moderately high temperatures becomes essentially different.

There are three chief kinds of commercial iron, viz. wrought-iron, steel, and cast-iron; the first contains the smallest, the last the highest, amount of carbon. Wrought-iron approximates most nearly both in composition and in properties to pure iron; it is tough, not very hard, and on being heated first becomes soft like wax or sodium before melting. This property is of the greatest importance for the technical working of iron, as it renders it possible to shape the metal and to unite different pieces without it being necessary to raise the temperature to the melting point of the metal. On the contrary, it is sufficient to heat to the temperature of softening (about 600°), so as to attain the object by pressing, rolling, and forging. The uniting of the two pieces of iron by pressure (hammering) is called "welding." The temperature necessary for this is bright red heat.

The properties of wrought-iron do not undergo essential change when it is heated and suddenly cooled. The character of *steel*, however, depends in the highest degree on such treatment.

Steel is iron which contains from 0·8 to 2·5 per cent of carbon, but is otherwise as pure as possible. The carbon is chemically combined with the iron, and this carburetted iron or iron carbide is alloyed with the rest of the iron. The result of the presence of this foreign ubstance is, in the first place, an appreciable sinking of the melting point; at 1400° steel is liquid and can be cast. Cast-steel is a metal onsisting of fine crystalline grains, which, like wrought-iron, softens efore melting, and can therefore be forged. By such treatment steel cquires a fibrous or sinewy character, similar to wrought-iron. If the teel is made red hot and then suddenly cooled, it becomes brittle, nd at the same time acquires its highest degree of hardness. It is hen so hard that it scratches glass, and is hence called "glass hard." f this steel is again carefully heated, all degrees of hardness can be mparted to it, for it increases in softness the longer or the higher it heated. This process is called the "tempering" of steel.

For the degree of tempering to be attained, use has been made om olden times of the colours which a bright steel surface acquires n being heated. At about 220°, the metal begins to oxidise in the r with a measurable velocity, and the oxide produced forms a thin coating on the metal. If the thickness of this coating is of the ord of a wave-length of light, the corresponding interference colour or the "colours of thin plates," begin to appear. Since the shortes of the visible waves, the violet, are first extinguished, the firs tarnish-colour to appear is the complementary colour, pale straw yellow. This passes through the colours orange, purple, violet, blu and finally becomes grey. To each of these colours there correspon a definite degree of hardness of the steel. Steel for tools to work iro is allowed to reach the yellow stage, for brass the purple-red stag while tools for wood are allowed to become blue. Although colo and hardness do not exactly correspond, still the correspondence sufficient for an experienced workman.

* In spite of numerous investigations, the theory of tempering h as yet scarcely been scientifically explained. Physical as well chemical processes seem to play a part here, for the tempering of ste recalls, on the one hand, the annealing of glass (p. 528), while, on th other hand, differences in the chemical combination of the carbon i the steel must be regarded as proved beyond doubt.

The great utility of steel in the arts is due to the diversity i the degrees of hardness which it can acquire. In the soft state it ca be shaped to any desired form, and the shaped objects can then b brought to any degree of hardness.

If the amount of carbon increases to from 4 to 5 per cent, th melting point of the iron becomes still lower, and the metal loses it toughness and the power of assuming the fibrous condition, but it sti retains the power of being tempered to a certain degree. Such iron called cast-iron.

Two kinds of cast-iron are distinguished, white and gray. Th former is obtained by quickly cooling; it is very hard and crystallin and contains the greater part of its carbon chemically combine When the cast-iron is slowly cooled, part of the carbon separates ou in fine laminæ as graphite, which imparts a gray colour to the iron. A the same time the metal becomes less hard and brittle, and the grai finer. In this condition cast-iron is used for innumerable purpose where ease in the shaping of the object by casting has to be take into account, and where the smaller resistance of the metal to pullin strain and bending is no essential drawback.

The Ions of Iron.—Iron forms two kinds of elementary as we as a large number of complex ions containing other elements alon with the iron. We shall in the first place treat of the former.

The elementary ions of iron are di- and trivalent; the former i called *diferrion*, the latter *triferrion*, and all the compounds which ar derived from the former are designated ferrous compounds, in contr distinction to those derived from the latter, which are designated ferri compounds. The ferrous compounds possess a similarity to those o magnesium, the ferric to those of aluminium.

Diferrion in the pure state is almost colourless. Most of the salts which contain diferrion exhibit a greenish coloration, which is usually regarded as that of the diferrion. It appears, however, to be due for the greatest part to the presence of a trace of triferrion, since dark coloured compounds of the two exist which even in very small amount produce the green coloration.

* Although diferrion does not absorb the visible rays to any great extent, it absorbs those of great wave length, the ultra-red or the heat rays, in a very pronounced degree. A vessel with parallel walls, filled with the solution of a ferrous salt, is the most effective means of freeing light rays (*e.g.* in projection apparatus) from the dark heat rays which are present, and thus of avoiding the harmful heating of the objects.

Diferrion has an "inky" taste, *i.e.* the taste of ink is due to the presence of iron, which is chiefly in the form of diferrion.

The salts of diferrion are, as already mentioned, very similar to those of magnesion, and are in many cases isomorphous with them; like the solutions, they have a greenish colour. The general reactions also are similar, but ferrous hydroxide is considerably less soluble than magnesium hydroxide. An essential difference is the tendency of diferrion to pass into triferrion, a reaction for which there is no counterpart in the case of magnesium.

Diferrion is very readily formed by treating metallic iron with acids. The conversion of metallic iron into diferrion then occurs, accompanied by the transformation of the hydrion into neutral, gaseous hydrogen; the reaction is therefore represented by the equation $Fe + 2H^{\cdot} = Fe^{\cdot\cdot} + H_2$. Of course the cations hydrion and diferrion cannot exist without there also being an equivalent quantity of anion present; for the reaction itself, however, the nature of the anion is of no importance so long as it has no influence on the state of ionisation of the hydrogen or of the iron.

* In the case of weak acids, the anion is for the most part united with hydrogen, and only a small part of the latter is in the ionic condition; the action of such acids is slower, being commensurate with the actual, not the potential concentration (p. 245) of the hydrion. The amount of iron which is ultimately dissolved, or the quantity of hydrogen evolved, depends, however, not on the degree of dissociation ut on the total amount of the acid hydrogen, because, in proportion s hydrion is used up, more is formed so long as the acid hydrogen is resent (p. 245).

Further, diferrion, *i.e.* a ferrous salt, is formed when ferrous sulphide s acted on by acids. We have already seen that this reaction is a nethod of obtaining sulphuretted hydrogen; it depends on the fact hat sulphuretted hydrogen is a weak acid, and ferrous sulphide a comaratively soluble sulphide, although its solubility is so small that it annot be detected by the ordinary analytical aids (p. 274).

A number of other reactions in which diferrion is formed will
discussed later.

The trivalent *triferrion*, $\text{Fe}^{\cdot\cdot\cdot}$, is also almost colourless.
aqueous solution, however, most of the ferric salts exhibit a yellow
brown-red coloration. This, however, is due not to triferrion b
to ferric hydroxide, which is present in the colloidal state in solutio
The formation of the latter regularly occurs from the fact that fer
hydroxide is a very weak base, and is therefore split off from its sal
by the hydrolytic action of the solvent water (p. 247). If much fr
acid is added, a part of the separated hydroxide is again convert
into ion, or into salt, and the solution loses more and more its re
brown colour.

* This is best seen by acidifying with nitric acid. Hydrochlo
acid produces a strongly yellow coloured and not a colourless liqu
because the undissociated ferric chloride, the amount of which
increased by the addition of chloridion (p. 441), has an intense yell
colour.

Triferrion is very readily formed in solutions from diferrion
means of *oxidising agents*. The divalent cation $\text{Fe}^{\cdot\cdot}$ thereby pass
into the trivalent ion $\text{Fe}^{\cdot\cdot\cdot}$. Oxidation of ions, therefore, is t
same as increasing the positive ionic charge. Since the sum of
positive and a negative charge is zero, increase of the positive char
is equivalent to diminishing the negative charge.

The opposite of oxidation is called *reduction*. In the above sen
therefore, reduction means the diminution of the positive or th
increase of the negative ionic charge. The following examples w
render this more clear.

The positive charge necessary for the conversion of diferrion in
the ferric state can be taken from another positive ion, which there
passes into the neutral (or less positive) state. This occurs, f
example, on mixing a ferrous salt with a silver salt; the former th
passes into a ferric salt, while the latter is converted into the neut
state, *i.e.* into metallic silver. The equation is, $\text{Fe}^{\cdot\cdot} + \text{Ag}^{\cdot} = \text{Fe}^{\cdot\cdot\cdot} + \text{A}$

This reaction takes place only when a comparatively large quanti
of diferrion is present; conversely, metallic silver dissolves in a sol
tion containing triferrion, thereby passing into argention: $\text{Fe}^{\cdot\cdot\cdot} + \text{Ag}$
$\text{Fe}^{\cdot\cdot} + \text{Ag}^{\cdot}$.

That the same substances exert opposite actions is due, in this
in every case, to the *action of mass*. The tendency of diferrion to pa
into triferrion is all the greater the greater its concentration, and t
less the concentration of the triferrion present at the same time, a
vice versa. In other words, the position which the mixture takes
oxidising and reducing agent, is a question of the relative concentr
tions of the two kinds of ions.

The conversion of a neutral substance into an ion with negati
charge is equivalent to the conversion of a positive ion into the neutr

state. It will therefore be possible to convert diferrion into triferrion by means of the former reaction.

As a matter of fact, this readily occurs when, for example, chlorine gas is passed into a solution of a ferrous salt. The reaction then is, $2Fe^{\cdot\cdot} + Cl_2 = 2Fe^{\cdot\cdot\cdot} + 2Cl'$. The diferrion passes into triferrion, and chloridion is formed at the same time.

In this case the reverse reaction cannot be measured or detected; it occurs, however, in the case of iodine. If a small quantity of iodine is mixed with much ferrous salt, there occurs the reaction $I_2 + 2Fe^{\cdot\cdot} = 2Fe^{\cdot\cdot\cdot} + 2I'$, just as in the case of chlorine. If, on the other hand, some iodidion is brought together with a large excess of triferrion, the reverse reaction occurs, $2Fe^{\cdot\cdot\cdot} + 2I' = 2Fe^{\cdot\cdot} + I_2$, and iodine is liberated.

To such changes in the ionic charge, all processes of oxidation and reduction can be attributed. The matter is, however, sometimes complicated by the fact that the particular substances are not completely dissociated, or are dissociated only to a very small extent. We shall soon have an opportunity of explaining by means of examples how the matter is then to be regarded.

Even on standing in the air, ferrous salts change into ferric salts. In this case the oxygen of the air takes part by forming hydroxidion with the water, and so yielding the negative ion, which must be simultaneously produced when the positive charge of diferrion is increased. The reaction can be expressed by the equation $4Fe^{\cdot\cdot} + O_2 + 2H_2O = 4Fe^{\cdot\cdot\cdot} + 4OH'$. The conversion of diferrion into triferrion is, therefore, actually effected by the free oxygen, and to this is due the designation of the process as one of oxidation. It is, therefore, a one-sided designation, and refers only to one of innumerable possible cases; for reasons, however, which now belong to the history of chemistry, a special importance was formerly attached to this process, and from it the general name was chosen.

In the case of the reaction just described, hydroxidion is formed from the oxygen with the co-operation of the water, and the solution contains hydroxidion or becomes basic. Salts in which hydroxidion is present along with other anions, have been called basic salts. Basic salts of triferrion, therefore, are formed in the conversion of ferrous nto ferric salts by means of free oxygen; these salts have the general formula $FeA_2(OH)$, where A is a monovalent anion. Since such salts are mostly difficultly soluble in water, we obtain the explanation why neutral ferrous salts on standing in the air become turbid, and deposit brown precipitates which are found to be basic salts like the above. n order to avoid this, the formation of hydroxidion must be prevented by the presence of hydrion. Acidified solutions of ferrous salts do not become turbid in the air.

What has been said holds generally. Whenever a cation is onverted by free oxygen into one of a higher valency, the liquid thereby becomes more basic. Conversely, a liquid becomes more acid when reductions are effected in it by means of hydrogen gas.

Ferrous Hydroxide.—When a solution of caustic potash or soda is added to the solution of a ferrous salt, a white, slimy precipitate of ferrous hydroxide, $Fe(OH)_2$, is precipitated, since the solubility of this substance in water is very slight. If, however, this experiment is carried out with ordinary solutions, a dark green and not a white precipitate is obtained. This is due to the fact that ferrous hydroxide unites extremely rapidly with free oxygen; the ferric hydroxide formed unites with the ferrous hydroxide to form a black compound, which has a greenish appearance when distributed in a finely divided state through the white precipitate. Even extremely small quantities of free oxygen are sufficient to produce this phenomenon, so that the solutions employed must be very carefully freed from air in order that the colour of the pure ferrous hydroxide may be seen.

* In order to free ferrous salts for these and similar purposes from triferrion, the solutions are warmed with metallic iron (iron filings). There then occurs the reaction $2Fe^{\cdot\cdot\cdot} + Fe = 3Fe^{\cdot\cdot}$, and triferrion passes into diferrion.

If the precipitate is exposed to the air, the surface immediately becomes dark greenish-black in colour, from formation of the above-mentioned double compound, and then red-brown, which is the colour of ferric hydroxide.

Ferrous hydroxide dissolves readily in dilute acids, with formation of the corresponding ferrous salt. It does not dissolve in alkalis, since it cannot form any anions.

It is, however, slightly soluble in salts of ammonium, similarly to magnesium hydroxide, although not so easily as this. This is due to its smaller absolute solubility, in virtue of which the solubility product is reached at smaller concentration of the diferrion. The ammoniacal solution, however, immediately becomes turbid in the air, and green-black flakes are precipitated from it and rapidly become brown. Oxygen is absorbed from the air, whereby diferrion is converted into triferrion, and the concentration of the hydroxidion at the same time increased. Since the solubility product of ferric hydroxide is very small, it separates out in the solid state.

This phenomenon does not occur when magnesium hydroxide is dissolved in ammonium salts, because magnesium cannot form a trivalent cation.

Freshly precipitated ferrous hydroxide (most cheaply a mixture of a ferrous salt and lime) can be used to remove oxygen from gases. Its action is fairly complete, although somewhat slow.

Ferrous Sulphate.—Of the ferrous salts, the sulphate is the best known and the most used. It occurs in bright green crystals with $7H_2O$, belonging to the monoclinic system. It cannot be directly regarded as isomorphous with magnesium sulphate, which also contains

$7H_2O$, because the latter salt is rhombic. Nevertheless, the two sulphates crystallise together in such a way that from solutions which chiefly contain ferrous sulphate, crystals containing magnesium, but of the form of the ferrous salt, are formed; while from solutions chiefly containing magnesium sulphate, crystals of the form of Epsom salts, but containing iron, are deposited.

The explanation of this phenomenon is that the two sulphates are dimorphous and at the same time isomorphous, for both can crystallise in rhombic as well as in monoclinic form. In the case of magnesium sulphate, the former is the more stable; in the case of ferrous sulphate, the latter. In the case of the mixed crystals, therefore, it depends on the ratio in which the salts are mixed which of the two forms is the more stable, the predominating salt always determining the form.

The popular name of ferrous sulphate is *iron vitriol*. The name "vitriol" is used to designate all sulphates of the iron group derived from divalent ions; thus there are also manganese, cobalt, and nickel vitriols. Copper sulphate, also, is called copper vitriol, although copper belongs to the next group; this is due to the fact that this salt is also partially isomorphous with the other vitriols.

Iron vitriol can be prepared by dissolving metallic iron or iron sulphide in dilute sulphuric acid and evaporating the liquid till it crystallises. It is, however, usually obtained in another way. Iron sulphide occurs very widely distributed in nature. In the moist state this is oxidised on contact with oxygen and passes into ferrous sulphate, according to the equation $FeS + 2O_2 = FeSO_4$. The rock containing iron sulphide is therefore spread out exposed to the air and moistened; in a short time, by extracting with water, large quantities of ferrous sulphate can be obtained from it. This method of preparation is so cheap that it was formerly the custom to use the iron vitriol for the preparation of sulphuric acid.

* In order to obtain sulphuric acid or "oil of vitriol" from iron vitriol, the salt was first heated in the air or "roasted," whereby it was converted into basic ferric sulphate: $4FeSO_4 + O_2 + 2H_2O = 4FeSO_4(OH)$. On being heated, this latter salt decomposes into sulphuric acid, sulphur trioxide, and ferric oxide, in accordance with the equation $2FeSO_4(OH) = Fe_2O_3 + H_2SO_4 + SO_3$. The resulting mixture of sulphuric acid and sulphur trioxide, on account of the presence of the latter, fumes in moist air (p. 284); it therefore constituted "fuming sulphuric acid," in contradistinction to the non-fuming acid prepared in the leaden chambers, which does not contain anhydride. Since this fuming acid was prepared in fairly large quantities at Nordhausen in the Harz, it was also called Nordhausen sulphuric acid.

At the present time this method is no longer used, as the manufacture of sulphur trioxide by the contact method has completely ousted all the others.

Like magnesium sulphate, ferrous sulphate unites with potassi sulphate and the salts isomorphous with this, to form monocli double sulphates of the type $K_2Fe(SO_4)_2 . 6H_2O$. The ammoni salt $(NH_4)_2Fe(SO_4)_2 . 6H_2O$, which crystallises well and does not oxid in the air, is used in analysis (cf. Manganese).

Other Ferrous Salts.—*Ferrous chloride*, $FeCl_2$, is a salt which very readily soluble in water, and which in solution rapidly oxidises the air; in the laboratory it is obtained in large quantities in the p paration of sulphuretted hydrogen from iron sulphide and hydrochlo acid. On concentrating the solutions it is obtained in the form greenish crystals containing $6H_2O$, which very readily become coat in the air with brown crusts of basic ferric salt.

Ferrous chloride is obtained in the anhydrous state by heati iron in a current of hydrogen chloride. The latter is decompos with liberation of hydrogen, and the ferrous chloride sublimes at bright red heat in white-grey, lustrous scales, which feel like ta The anhydrous salt dissolves in water with great evolution of heat.

Concerning *ferrous bromide* and *ferrous iodide*, there is nothing spec to note. The aqueous solutions of these salts are readily obtained bringing the free halogens together with excess of metallic iron; t salts are very readily soluble.

Ferrous carbonate, $FeCO_3$, occurs naturally as a valuable iron o *spathic iron ore.* It crystallises in rhombohedra which are isom phous with those of calc-spar and of magnesite; in the pure state is almost colourless, but is generally coloured yellow-brown fro incipient oxidation. From aqueous solutions of ferrous salts solub carbonates precipitate it as a greenish-white substance, which readi dissolves in acids, with effervescence, and which also becomes rath rapidly brown owing to oxidation.

Ferric Hydroxide.—By the addition of bases to solutions ferric salts, ferric hydroxide, $Fe(OH)_3$, is obtained as a brown, flocc lent precipitate, which is very slimy when precipitated in the col If the liquid is heated along with the precipitate, the latter acquires firmer character, and can be readily filtered.

Ferric hydroxide is a very weak base, and is practically insolub in water. In acids it is soluble when freshly precipitated, and if has not been heated; it passes, however, into less soluble forms eve on standing for some time in the heat, partial anhydride formatio presumably occurring. On being heated to a red-heat it loses wat and is converted into ferric oxide, Fe_2O_3, according to the equatio $2Fe(OH)_3 = Fe_2O_3 + 3H_2O$. This ignited iron oxide is almost insolub in acids, and passes into solution only on being warmed for days wit concentrated hydrochloric acid; it dissolves more quickly when it at the same time reduced to ferrous salt.

Ferric hydroxide possesses the property to a very high degree forming colloidal solutions. These are obtained by dissolving freshl precipitated ferric hydroxide in a concentrated solution of ferric chloride, whereby soluble basic salts are formed, and dialysing this through a partition of parchment paper into pure water. The aqueous solutions of ferric chloride, like those of all other ferric salts, are partially hydrolysed into free acid and colloidal ferric hydroxide. Since hydrochloric acid diffuses very quickly, while ferric hydroxide and basic ferric chloride can hardly penetrate the parchment paper, the hydrochloric acid present first of all passes out. The chemical equilibrium of hydrolysis is thereby disturbed, more hydrochloric acid must be split off, and this is in turn removed by diffusion. These reactions continue until finally only or almost only colloidal ferric hydroxide is left in the dialyser.

The solution so obtained is of a dark blood-red colour, and exhibits the characteristic properties of colloidal solutions in the most distinct manner. It does not possess electrical conductivity to any considerable extent; its boiling point and freezing point, also, differ only inappreciably from those of pure water. Addition of electrolytes precipitate it, the ferric hydroxide separating out as a flocculent mass. Chemical reactions do not take place with it, or do so only very slowly; more especially, it exhibits none of the analytical characteristics of the ferric salts, which will be mentioned later, since it does not contain triferrion. On standing with hydrochloric acid it gradually passes into a liquid possessing the properties of the solution of ordinary ferric chloride.

Solutions of colloidal ferric hydroxide are prepared in the above manner for medicinal purposes, and are sold under the name *ferrum oxydatum dialysatum* (dialysed iron).

Both hydroxide and oxide of iron occur in nature; both are important iron ores, and are called brown iron ore and hæmatite respectively. The former occurs in brown-black lustrous masses which, on being ground, yield a yellow-brown powder. Iron oxide crystallises in rhombohedra which are isomorphous with those of corundum (p. 551), and have a black metallic appearance; in this form it is called iron glance. The concretionary iron oxide (kidney ore) has a black-red appearance; on being ground, both varieties of the oxide yield a red powder, whereby it is readily distinguished from the native ferric hydroxide, to which it otherwise appears somewhat similar.

Iron oxide and hydroxide are extremely widely distributed in nature. In the primitive rocks, iron regularly occurs in the form of silicate; in the weathering, the silicic acid is removed and the hydroxide remains. This mixes with all sedimentary rocks, and imparts to them a yellow-brown to red colour. When reducing actions occur, as, for example, through admixture with organic substances, the ferric hydroxide is reduced to the dark-coloured compound mentioned on p. 568, and this gives a grey-blue or greenish-blue colour to the particular substances. This colour is frequently seen in the case of clays containing iron ; when these are “ fired ” the organic substanc is destroyed, and the iron passes into ferric oxide, whereby the pr viously blue clay becomes of a red colour.

Ferric hydroxide resembles aluminium hydroxide in many respect especially in the fact that the salts of both have a similar compositio and are also mostly isomorphous. Like aluminium hydroxide, ferri hydroxide is completely precipitated by ammonia from solutions ferric salts. It differs, however, from aluminium hydroxide in the fa that it is not dissolved by strong bases ; in fact a method of separatin the two hydroxides can be based on this difference. The metho however, is not very exact, for the difference, or the inability of ferri hydroxide to form anions containing oxygen (p. 551), is only one degree ; in very concentrated solutions of the alkali hydroxides, ferri hydroxide dissolves quite appreciably, and for this reason caustic alkali prepared in iron boilers almost always contain iron. On diluting th solutions, the compound decomposes and the ferric hydroxide is gradually deposited as a brown precipitate on the bottom of the vessel.

In the presence of many organic substances, such as tartaric aci sugar, glycerine, etc., all of which contain several hydroxyl group ferric hydroxide is not precipitated by alkalis from solutions of ferri salts ; on the contrary, clear brown liquids are formed which exhibi the reactions of iron only imperfectly. The description of the compounds hereby produced belongs to organic chemistry ; they are salt like compounds in which the iron is present not as cation but as par of a complex anion. They have received mention here from the fac that they are extremely readily formed, and when formed they rende the analytical detection and the precipitation of the iron more difficult In such cases the organic substance must be destroyed, which is mos easily done by strongly heating.

Magnetic Iron Ore.—Ferric oxide unites with ferrous oxide t form a compound which occurs abundantly in nature, and is a ver valuable iron ore : $Fe_2O_3 + FeO = Fe_3O_4$. It is called magnetic iro ore, as it frequently exhibits a strong natural magnetism ; the chemica name is ferrosoferric oxide.

Magnetic iron ore crystallises in regular octahedra, and is isomorphous with spinel (p. 552), which consists of aluminium oxide an magnesium oxide, $Al_2O_3 + MgO$. As can be seen, the two compound are constituted after the same type, since both contain one combinin weight of a monoxide, MO, to one of a sesquioxide, M_2O_3. In the present case, however, iron is the only metal present, its divalent form taking the place of magnesium, and its trivalent form that of aluminium In magnetic iron ore, therefore, both the isomorphic relations com simultaneously into force.

If ferrous salt and ferric salt be mixed in such proportions tha there is twice as much iron in the case of the latter salt as in th former, and the mixture be poured into excess of caustic soda, a blac granular precipitate is obtained, which may be looked upon as a ydroxide of the above compound. A salt-forming base, also, appears o exist; this is a compound of ferrous and ferric hydroxide, and o it is due the greenish colour of the ferrous salts. This compound, owever, if it exists, is very unstable, its salts decomposing almost ompletely into mixtures of ferrous and ferric salts.

Ferric Salts.—*Ferric chloride*, $FeCl_3$, is obtained by heating iron n a current of chlorine. It then sublimes as dark-green crystals with metallic lustre, and is much more easily volatile than ferrous chloride.

These crystals dissolve in water with great rise of temperature, nd yield a yellow-brown solution from which the anhydrous salt canot be again obtained by evaporation and heating. Four different ydrates containing from $12H_2O$ to $4H_2O$ crystallise out, according o the temperature, and on attempting to drive off the last traces f water by heating, hydrogen chloride is eliminated at the same ime, and iron oxide remains behind.

Hydrated ferric chloride can be obtained by dissolving ferric oxide n hydrochloric acid, by passing chlorine into a solution of ferrous hloride, and in other ways. The solution is evaporated until the mount of water corresponds to $FeCl_3 + 6H_2O$; on cooling, it crystalises to yellow crystals of the hydrated salt, which dissolves very eadily in water. The 43·5 per cent aqueous solution of this salt is fficinal.

Ferric chloride also dissolves in other solvents, like alcohol and ther. The solutions are yellow; yellow is therefore the colour of erric chloride in the undissociated state.

The aqueous solutions of the salt react strongly acid, since, on ccount of the feebly basic properties of ferric hydroxide, the salts re to some extent hydrolytically dissociated. The hydrolysis inreases with the dilution and with rise of temperature. It betrays tself to the eye by the fact that the yellow colour of the undissociated erric chloride disappears and gives place to the red-brown colour of he colloidal ferric hydroxide which is formed.

* These properties can be made very clear by means of some imple experiments. Two equal small portions of a fairly dilute olution of ferric chloride are taken, and to one there is added so much ater that it becomes almost colourless. If to the other portion an qually large volume of strong hydrochloric acid is added, a liquid of strong yellow colour is obtained. Owing to the great concentration f chloridion in the second case, the electrolytic dissociation of the erric chloride is so greatly diminished that the yellow colour of the ndissociated substance makes its appearance.

* A solution of ferric chloride, diluted almost to colourlessness, is ivided into two portions, and these are placed in equally wide testubes. If the one portion is heated the solution becomes of a browned colour, hydrochloric acid and colloidal ferric hydroxide being

formed by hydrolysis. This coloration persists also when the heat tube is placed in cold water, so that both portions of the origin liquid have the same temperature. If, however, the two tubes a kept side by side for several days, the colour of the solution which ha been heated becomes weaker, and ultimately both specimens are of t same colour. This is due to the fact that the hydrolysis, which wa greatly increased by warming, diminishes at a low temperature, t hydrochloric acid and the ferric hydroxide being again converted in ferric chloride, or into triferrion and chloridion.

Ferric Bromide and Ferric Iodide.—While the bromine co pound of the ferric series possesses no special interest, interest attach to the iodine compound. It has already been mentioned (p. 567) th in this case the components exist to a measurable extent in chemic equilibrium. If to a solution of ferrous iodide, FeI_2, as much free iodi is added as corresponds to the formula FeI_3, it passes, indeed, in solution, but the solution still exhibits the reactions of free iodine, a at a higher temperature the latter volatilises from it. The reactio $2FeI_2 + I_2 = 2FeI_3$, therefore, does not take place completely, but t reverse reaction can also occur to a large extent. If the iodine removed from the equilibrium, the reverse reaction must take pla more and more, and ferrous iodide must ultimately remain. Th reaction, however, becomes increasingly difficult the more iodine removed from the solution.

Writing the ions which are present, the equation runs $2Fe^{\cdot\cdot\cdot} +$ $2I' = 2Fe^{\cdot\cdot} + I_2$, and the reader may be referred to the consideratio set forth on p. 567.

* This reaction is used for analytical purposes for the separatio of iodine from chlorine and bromine. For this purpose excess of ferric salt is added to a solution containing the halogens as ions, an the liquid is distilled. The iodine then passes off with the stea while the bromidion and chloridion remain behind. The volatilise iodine is absorbed in a solution of potassium iodide, and titrated wi thiosulphate.

* A mixture of ferrous and ferric iodides is obtained as a intermediate product in the preparation of potassium iodide. Iodi and iron, in the proportions 3Fe : 8I, are mixed with water, whereb all is dissolved, and the solution is precipitated with caustic alkali o potassium carbonate. Potassium iodide is formed in the solution, an the iron is deposited as the black ferrosoferric oxide (p. 572), whic can be more easily filtered and washed than the other oxides of iron.

Ferric Fluoride, FeF_3, is distinguished by the fact that it i extremely slightly dissociated into its ions, and does not, therefor exhibit the reactions of triferrion and fluoridion. It is a difficult soluble, white compound, which forms with the alkali fluorides com pounds of the type of cryolite (p. 554), constituting the alkali salts o a trivalent fluoferranion, FeF_6'''.

Ferric Sulphate, $Fe_2(SO_4)_3$, is obtained by adding to a solution f ferrous sulphate half as much sulphuric acid as is therein contained, nd evaporating the solution with addition of nitric acid (to oxidise the iferrion to triferrion). After heating the residue there is finally btained a yellowish-white powder, which apparently does not dissolve ı water. If left for some time under water, however, it dissolves in bundance, and fairly concentrated solutions can be prepared. It is a ılt, therefore, which has a very small solution velocity.

The solutions appear brown-red, but the colour is all the paler the ıore free acid is added. This is due to hydrolysis, which is diminished y free acid. The hydrolysis again increases when the solution is reatly diluted.

Ferric sulphate crystallises along with potassium or ammonium ılphate to form alums, which are called iron alums. The salt ystallises in octahedra, which generally appear violet (probably owing) the presence of a trace of manganese). When pure the salt is lmost colourless, tinged with yellow. Iron alum is generally used here it is necessary to employ a ferric salt in cases where ferric ıloride, for some reason, cannot be used.

Ferric Thiocyanate, $Fe(SCN)_3$, is exceedingly soluble in water, nd in the undissociated state is of a deep red-brown colour. The nallest amount of triferrion, therefore, can be detected by adding an xcess of thiocyananion (*e.g.* potassium thiocyanate) to the solution. ince the reaction is due to the undissociated ferric thiocyanate (for oth thiocyananion and triferrion are colourless, or only slightly loured), it will, *ceteris paribus*, be all the more distinct the greater the nount of the undissociated compound present.

* This object is, in the first instance, attained by a large excess of iocyananion. If to a solution containing only a very little triferrion, nly an equivalent amount of thiocyananion is added, the coloration roduced is very feeble; it becomes more pronounced the more the ncentration of the thiocyananion is increased. Further, the reaction ecomes more distinct if the liquid is shaken with ether. Ferric iocyanate in the undissociated state is soluble in ether; the undis- ociated portion, therefore, passes for the greater part into the ether, fresh amount of the compound is formed in the aqueous solution, and is also goes into the ether. When equilibrium is finally established ere is much more undissociated ferric thiocyanate in the ether than ere was previously in the aqueous solution. As a consequence, the nsitiveness of the reaction is correspondingly enhanced.

* If a concentrated solution of sodium or ammonium sulphate is lded to a liquid coloured red with ferric thiocyanate, the red colour ecomes weaker, and finally disappears. This is due to the fact that ving to the presence of a large amount of sulphanion, the triferrion used up for the formation of undissociated ferric sulphate, which is t coloured. The salts of monobasic acids do not act so strongly,

since the ferric salts of the polybasic acids are generally much less dissociated than those of the monobasic acids. Fluorides act very strongly (cf. p. 574).

Other Ferric Salts.—*Ferric acetate* is an unstable salt, the behaviour of which is, for analytical purposes, of interest. If sodium acetate (or acetanion in any other form) is added to the solution of a ferric salt, the liquid becomes dark red in colour, owing to the formation of undissociated ferric acetate. This reaction is used as a reagent for acetic acid, but similar colorations are produced by a number of other anions, so that the reaction is not unequivocal. If the red solution is heated it becomes turbid, and a precipitate of basic acetate is formed, which contains all the iron. In this way iron (in the ferric state) can be precipitated from acid solutions, which is of importance for many separations.

* If the liquid is again allowed to become cold in contact with the precipitate, it slowly regains its red colour, and the iron begins to pass into solution. When, therefore, an exact separation is required, the precipitate must be filtered hot.

* The explanation of this reaction is the same as in the case of aluminium acetate (p. 558). Since acetic acid is a weak acid (the hydrion of which is still further diminished by the excess of acetanion from the sodium acetate added), hydrolysis largely occurs, and in the heat this goes so far that ferric hydroxide, or basic acetate, is precipitated. The reverse process takes place at a lower temperature on account of diminution of hydrolysis.

Ferric Phosphate, $FePO_4$, is precipitated from a solution of a ferric salt, acidified with acetic acid, by the addition of sodium phosphate, as a white, slimy precipitate which, unlike most of the other phosphates, is not appreciably soluble in acetic acid. This property is also made use of in analysis.

Sulphur Compounds of Iron.—If iron and sulphur are heated together a black mass of the composition FeS is formed. This we have already got to know as the starting substance in the preparation of sulphuretted hydrogen. The compound can be prepared in any desired amount by raising the end of an iron bar to a red heat, lowering this into a large crucible, and adding sulphur in lumps. The two elements combine with so great a rise of temperature that the iron sulphide is melted, and the preparation can be continued by simultaneously adding more sulphur and pushing the iron bar farther in.

* A hydrated sulphide of iron of a black colour is formed when sulphur and iron filings are mixed in the proportions 32 : 56, moistened with water, and allowed to stand. The reaction commences slowly, but is accelerated by the heat produced, and in the case of large quantities it may be so violent that the mass becomes incandescent. Such experiments were formerly often made in imitation of volcanic phenomena. Since, however, the lava of the natural volcanoes

does not consist of iron sulphide, it is only a case of external resemblance.

Iron sulphide is readily decomposed by acids, with formation of ferrous salt and sulphuretted hydrogen (p. 266), and it is therefore not formed when sulphuretted hydrogen is passed into solutions of ferrous salts. By means of ammonium sulphide, however, a black precipitate of hydrated iron sulphide is formed in ferrous solutions; when finely divided it appears green-black, and forms a very sensitive reaction for iron. Iron sulphide rapidly oxidises in the air, ferrous sulphate being first formed (p. 569), so that it cannot be washed on the filter without beginning to dissolve.

Iron sulphide occurs native as magnetic pyrites in yellow-brown masses, with a metallic lustre. These have very nearly the composition of the simple iron sulphide, but always contain a slight excess of sulphur. How this deviation from the law of constant proportions is to be interpreted has not yet been explained.

A sulphide of iron corresponding to ferric oxide, whose composition would therefore be Fe_2S_3, is not known. This is a conspicuous exception to the otherwise very general rule that the oxygen and the sulphur compounds have corresponding composition. The anomaly becomes all the greater through the fact that the sulphide of iron occurring most frequently in nature has the composition FeS_2, to which again no oxygen compound corresponds.

If sulphuretted hydrogen is passed into a solution of a ferric salt a white turbidity is produced, and the liquid becomes acid. The turbidity is finely divided sulphur, and the reaction consists in the triferrion present being reduced to diferrion by means of the sulphuretted hydrogen. The process can be most simply regarded as an interaction between negative sulphidion and positive triferrion, whereby the former entirely loses its charge, the latter partially: $2Fe^{\cdot\cdot\cdot} + S'' = 2Fe^{\cdot\cdot} + S$. The hydrion belonging to the sulphuretted hydrogen is the cause of the acid reaction.

The double sulphide of iron, FeS_2, is called, as a mineral, iron pyrites, and forms brass-yellow crystals belonging to the regular system, which are of very frequent occurrence (as enclosures, for example, in almost all coal). Iron pyrites is an important starting substance for the preparation of sulphuric acid; for this purpose it is roasted, *i.e.* heated with access of air, in specially constructed furnaces, when it burns without further heating to ferric oxide, which remains behind, and sulphur dioxide, which escapes: $4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$. When heated with exclusion of air it loses a part of its sulphur.

Ferric Acid and Ferrates.—When a mixture of iron and nitre is heated it burns with energetic reaction. If the product after being cooled (not while hot) is dissolved in water, a dark-red coloured liquid is obtained, which, however, does not keep well, but rapidly becomes colourless, thereby depositing flocculent masses of ferric oxide. A liquid having a similar appearance is obtained by electrolysing a solution of caustic potash with an anode of cast-iron, and also when chlorine is passed through a solution of caustic potash in which ferric hydroxide is present.

The red colour is due to a small quantity of salt of the composition K_2FeO_4, and which therefore contains the anion FeO_4''. The salt is readily decomposable in solution, and loses oxygen. On acidifying, the decomposition occurs instantaneously. The potassium ferrate is somewhat more stable in the solid state; it is isomorphous with potassium sulphate, K_2SO_4.

Cyanogen Compounds of Iron.—It has already been mentioned, when describing potassium cyanide, that this compound unites with iron to form good crystallising and stable compounds. These prove to be salts of complex anions, which, although they contain iron, do not give the usual iron reactions. Since the "iron reactions" are the reactions of diferrion and triferrion, we must conclude that these are not present, or are so only in infinitely small concentration.

The compounds are very readily obtained by allowing an alkali cyanide to act on iron or an iron compound. In the case of metallic iron the reaction takes places with evolution of hydrogen and formation of potassium hydroxide, in accordance with the equation $6KCN + Fe + 2H_2O = K_4Fe(CN)_6 + 2KOH + H_2$. If an iron salt is taken, the corresponding potassium salt is formed. In this case it is a matter of indifference whether the iron salt is soluble in water or not, since potassium cyanide has under all conditions a solvent action.

On concentrating the solution the salt is obtained in bright yellow hydrated crystals of the composition $K_4Fe(CN)_6 + 3H_2O$, which yields a pale yellow solution. As the formula shows, it is the potassium salt of a tetrabasic acid, $H_4Fe(CN)_6$, which is called *hydroferrocyanic acid;* the potassium salt is accordingly called *potassium ferrocyanide.* It is better known under the old name *yellow prussiate of potash.*

The ferrocyanides exhibit the reactions of cyanidion just as little as they do those of iron; more especially, they are not poisonous, whereas cyanidion is so in a high degree. This is a further proof that the constituents of this salt do not exist side by side, as in the case of ordinary double salts, but have united to form a new anion $Fe(CN)_6''''$.

If strong hydrochloric acid is added to a concentrated solution of the potassium salt, a white, generally somewhat bluish coloured crystalline precipitate is deposited of the composition $H_4Fe(CN)_6$, which is therefore hydroferrocyanic acid. This readily dissolves in water, yielding a strongly acid liquid, which is, however, not very stable, but undergoes a complex decomposition, with deposition of a blue precipitate.

The hydroferrocyanic acid unites with all bases to form the corresponding salts, of which those of the alkali metals are readily soluble; those of the alkaline earth metals are, some of them, rather difficultly soluble, and those of the heavy metals are practically insoluble. The latter mostly exhibit conspicuous colours, and serve therefore for the detection of some of the metals.

If a solution of potassium ferrocyanide is added to a solution containing diferrion, a white precipitate is formed which is the ferrous salt of hydroferrocyanic acid, $Fe_2Fe(CN)_6$. For this precipitate the same holds good as was stated for ferrous hydroxide (p. 568). It can be obtained white only when oxygen is excluded, and it is coloured blue by the smallest amount of free oxygen or of an oxidising agent, the ferric compound being formed which will be described presently. This precipitate is therefore used to prove the absence of free oxygen, *e.g.* in gases, and for this purpose it forms one of the most delicate tests.

It is to be noticed that the two portions of iron in this compound vary in their behaviour. Whereas two-thirds of it has entered the compound as diferrion, and behaves accordingly, the last third reacts differently. If, for example, caustic potash is poured over the white precipitate, the latter is decomposed; ferrous hydroxide is deposited, and potassium ferrocyanide remains in the solution. Two-thirds of the iron, therefore, passes into the precipitate, the last third passes into solution; the solution of potassium ferrocyanide is not affected by the caustic potash.

If the ferrocyanidion is brought together with triferrion (instead of diferrion) the ferric salt of hydroferrocyanic acid is formed. Since triferrion is trivalent and ferrocyanidion is tetravalent, the normal salt requires four combining weights of triferrion to three combining weights of ferrocyanidion, and the formula of the salt is $Fe_4[Fe(CN)_6]_3$, or in sum $Fe_7(CN)_{18}$. The compound is of a deep blue colour, the colour being recognisable even in very small quantity, so that it forms a very sensitive reaction for triferrion. The compound is manufactured on account of its fine colour, and is placed on the market under the name of Prussian blue. In using it, it must be noted that although it is not acted on by acids, it is decolorised and decomposed by bases.

This decomposition by bases depends on processes which are perfectly similar to those above described. On treating the ferric ferrocyanide, as this salt must be called, with caustic potash, potassium ferrocyanide is again formed, and ferric hydroxide is precipitated: $Fe_4[Fe(CN)_6]_3 + 12KOH = 3K_4Fe(CN)_6 + 4Fe(OH)_3$. Here again the two portions of iron in the compound behave differently.

* Similar processes are made use of in the preparation of potassium ferrocyanide on the large scale. In the gas-works the sulphuretted hydrogen is removed from the impure coal-gas by passing it over a mixture of lime and ferrous sulphate; the sulphuretted hydrogen thereby forms iron sulphide. At the same time, ammonium cyanide is present in small amount in the crude gas, and this is converted by

the purifier into calcium cyanide and calcium ferrocyanide. This salt is extracted with water, if necessary with the addition of lime, and converted into the potassium salt by means of potassium chloride and potassium carbonate. The iron sulphide is again converted into ferrous sulphate by spontaneous oxidation in the air, and on the addition of lime, the purifier is again fit for use, or is "regenerated."

The method of detecting small quantities of hydrocyanic acid mentioned on p. 414, depends on the reactions just described. To the solution is added excess of caustic potash or soda, in order to form an alkali cyanide, and an iron salt is then added; potassium ferrocyanide is thereby formed (p. 578). The iron salt must be in excess. If the liquid is now acidified, the ferrocyanidion reacts with the triferrion, which passes into solution, and Prussian blue is precipitated. If the amount of cyanide is very small, the Prussian blue remains in colloidal form in solution, and a clear blue liquid is obtained.

While ferrocyanidion is very stable in the cold, it decomposes at a red heat, and is converted into simpler compounds. Potassium ferrocyanide blackens on being fused, nitrogen is evolved, iron carbide separates out, and the fused mass consists essentially of potassium cyanide: $K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2$. This was formerly the method of preparing potassium cyanide, but a third of the cyanogen is thereby lost. In order to avoid this, the carefully dried potassium ferrocyanide is now fused with sodium. Iron is then deposited, and a mixture of potassium and sodium cyanide is obtained; for most purposes this is just as suitable as the pure potassium cyanide, because in its applications it is the cyanidion and not the potassion which is of importance. The reaction is represented by the equation $K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe$. The readily fusible melt can be much more readily poured off from the deposited iron than the potassium cyanide could, in the old method, from the iron carbide.

Under the influence of acids also hydroferrocyanic acid decomposes at a gentle heat. When potassium ferrocyanide is distilled with dilute sulphuric acid, hydrogen cyanide passes over, while about half of the cyanogen remains behind in the form of a bright blue compound which is closely related to ferrous ferrocyanide (p. 579). The decomposition is too complicated to be represented by a single equation. At the present day, when nearly pure potassium cyanide can be readily obtained, it is more simple to decompose this with dilute acids when it is desired to prepare hydrocyanic acid.

Ferricyanide Compounds.—If the solution of potassium ferrocyanide is treated with oxidising agents, it becomes of a dark brown-green colour, and on concentrating the solution a dark-red coloured anhydrous salt crystallises out. This has the composition $K_3Fe(CN)_6$, and readily dissolves in water with an intense yellow colour. The solution, however, decomposes rather quickly, although the dry salt is stable.

If chlorine be used as the oxidising agent, the reaction can be written thus: $2K_4Fe(CN)_6 + Cl_2 = 2K_3Fe(CN)_6 + 2KCl$, or if the participating ions only are written, $2Fe(CN)_6'''' + Cl_2 = 2Fe(CN)_6''' + 2Cl'$.

As can be seen from the above formulæ, the anion of the new salt has the same composition as that of the old one, viz., $Fe(CN)_6$, and the difference consists only in the fact that the new anion is trivalent while the old one is tetravalent. The difference is therefore quite similar to that between diferrion and triferrion, which also have the same composition and differ from one another in the charge of their ions. Since an increase in the positive charge is equivalent to a decrease of the negative, the following ions correspond to one another:—

Diferrion $Fe^{\cdot\cdot}$ and Ferrocyanidion $Fe(CN)_6''''$
Triferrion $Fe^{\cdot\cdot\cdot}$ and Ferricyanidion $Fe(CN)_6'''$.

This correspondence is also given expression to in the names.

The general properties of the ferricyanides are similiar to those of the ferrocyanides. In these compounds, also, neither the reactions of triferrion nor those of cyanidion can be detected. A difference, however, is shown in the reactions with iron salts.

If diferrion and ferricyanidion come together, a blue precipitate is formed which is very similar to Prussian blue, but has a somewhat different composition. For the salt which is formed, ferrous ferricyanide, has the composition $Fe_3[Fe(CN)_6]_2$, or in sum $Fe_5(CN)_{12}$. It contains, therefore, 2·40 combining weights of cyanogen to one of iron, while Prussian blue contains 2·53 combining weights of cyanogen to one of iron.

No precipitate is produced with ferric salts, but the liquid only becomes somewhat darker in colour. Ferric ferricyanide is soluble in water, and in the undissociated state is dark coloured.

By means of concentrated hydrochloric acid, hydroferricyanic acid, $H_3Fe(CN)_6$, can be liberated from the solution of its salts, and can be obtained in brown needles which are readily decomposable and very readily soluble in water.

The ferrous compound is decomposed by alkalis in the same way as Prussian blue, for potassium ferrocyanide and ferric hydroxide are formed, and not potassium ferricyanide and ferrous hydroxide, as one would expect. This is due to the fact that the potassium ferricyanide primarily formed is reduced by the ferrous hydroxide, which is a very strong reducing agent, to the ferrous compound, the ferrous hydroxide being converted into ferric hydroxide.

Other Complex Compounds.—With many other substances besides cyanogen, iron is capable of forming complex compounds which contain compound ions in which iron is present, and therefore do not give the reactions of iron, or do so only very incompletely. The description of most of these substances must be omitted here;

only a few of them, which, for some special reason, chiefly analytical, are of importance, can be mentioned here.

In the first place, there must be mentioned the compounds which are formed when *nitric oxide* or higher oxygen compounds of nitrogen are brought together with ferrous salts. The latter compounds are, then reduced to nitric oxide, and this unites with the diferrion to form the compound ion $FeNO^{\cdot\cdot}$. This is, however, rather unstable, for it undergoes decomposition even on boiling the solution, nitric oxide escaping and diferrion being again formed. This behaviour is made use of for the preparation of pure nitric oxide from mixed gases. On it also analytical methods of detecting nitric oxide and the higher oxy-compounds of nitrogen depend (p. 323).

Further, the complex iron anions can be formed by the compounds of ferric hydroxide with organic (and also with some inorganic) substances containing hydroxyl, which were mentioned on p. 572. They are recognised by the fact that their solutions are not precipitated by alkalis.

Oxalates of Iron.—The oxalates of iron, which have from all time been regarded as a chemical puzzle on account of the differences of their colour from the ordinary colours of the ferrous and ferric compounds, must also be reckoned among the complex compounds.

When free oxalic acid is added to a ferrous salt, a crystalline precipitate of ferrous oxalate, difficultly soluble in water, is deposited. Unlike the other ferrous salts, this is not greenish but orange coloured, like a ferric salt. It dissolves with a strong yellow-red colour in an excess of potassium oxalate, and from this solution the salt $K_2Fe(C_2O_4)_2$ can be obtained in crystals. In the solution, therefore, a salt of the complex ferro-oxalanion, $Fe(C_2O_4)_2''$, is formed.

* The solution of potassium ferro-oxalate, which is prepared at the moment it is to be used by mixing solutions of ferrous sulphate and normal potassium oxalate, is, on account of its powerful reducing properties, used in photography for developing silver bromide plates.

Moist ferric hydroxide readily dissolves in oxalic acid to yield a liquid which, unlike the other ferric salts, is coloured green. The colour is, however, emerald green and not pale green, like that of the ferrous salts. From the solution, badly crystallising ferric oxalate can be obtained, which readily decomposes. If, however, another oxalate is added, fine crystalline, green coloured salts of the complex ferro-oxalanion, $Fe(C_2O_4)_3'''$, are obtained, *e.g.* $K_3Fe(C_2O_4)_3$.

The solutions (also coloured green) of these salts possess in a high degree the property of sensitiveness to light. In sunlight, a solution of ferric oxalate almost instantaneously deposits a yellow precipitate of ferrous oxalate, and carbon dioxide is evolved: $Fe_2(C_2O_4)_3 = 2Fe(C_2O_4) + 2CO_2$. The salts of ferrioxalic acid behave in a similar manner, being converted into the corresponding salts of ferro-oxalic acid: $2K_3Fe(C_2O_4)_3 = 2K_2Fe(C_2O_4)_2 + K_2C_2O_4 + 2CO_2$. These phenomena are made use of for the production of photographs, especially of platinum pictures, a graded reduction being allowed to take place by exposure under a "negative," and the potassium ferro-oxalate thus produced being used for the reduction of platinum from a compound present. The solution has also been used as a chemical photometer, *i.e.* an apparatus for measuring the strength of the chemically active light. Apart from other objections, the results are of little value, from the fact that every sensitive substance has its particular range of light waves which it absorbs and makes use of for chemical reactions. There is, therefore, no such thing as a "chemical intensity of light" in the absolute sense, and every chemical photometer indicates the strength of only a definite range of rays of the light subjected to examination, this range being dependent on the nature of the photometer.

Iron Carbonyls.—Carbon monoxide combines with iron to form very remarkable compounds, which are slowly formed when the two components come into contact at the ordinary or at a slightly higher temperature. Various substances are hereby formed, containing from 4 to 7 CO to 1 Fe; they are readily volatile, so that they mix in the gaseous state with the excess of carbon monoxide. Their velocity of formation is so small that even by using finely divided iron with a large surface only very small amounts are formed, which are difficult to isolate and to prepare pure.

* Appreciable amounts of these compounds are formed in iron pipes which convey gas rich in carbon monoxide, especially when the conduits are long and the carbon monoxide has, therefore, time to unite with the iron. While for ordinary purposes these traces of iron in the gas are of no importance, they have proved very inconvenient in the application of such gas for incandescent light, as the iron oxide which is produced in the combustion is deposited on the incandescent mantles, and impairs their illuminating power.

A better known example of such compounds will be described under nickel.

Catalytic Actions of Iron.—Both in the ionic state and in numerous compounds, iron frequently exercises a very considerable catalytic influence, especially on oxidation processes. To observe this it is only necessary to mix dilute solutions of hydrogen peroxide and hydrogen iodide, or better, potassium iodide plus acetic acid. A reaction slowly occurs in which iodine is liberated and can be rendered visible by means of starch. If quite a small amount of any ferrous salt is added, the blue coloration occurs incomparably more quickly. A similar accelerating action has been proved in the case of many other reactions.

At the present time, no regularities of a more general nature are known respecting these relations. It is of importance, however, to be aware of them, since the physiological importance of iron probably depends on them. The presence of iron has been detected both in the red blood corpuscles and in the green colouring matter of the assimilating plant cells (*i.e.* those which reduce carbon dioxide in light), and although at the present time the laws of these relations cannot be stated, nevertheless, the fact above mentioned indicates an important direction for investigation.

Metallurgy of Iron.—As metallic iron does not occur native to any great extent, the very large quantities of this metal which are used in the industries must be manufactured from its compounds. For this purpose the oxygen compounds, which are reduced with charcoal, are almost exclusively used.

This reduction is carried out chiefly in the blast-furnace, which is an elongated, egg-shaped space enclosed by masonry; into this alternate layers of iron ore and coal, along with the additions necessary for the production of a readily fusible slag, are introduced from the top. In the lower part of the furnace there is a narrow cylindrical space into which heated air is blown, and in which the fused iron collects.

The changes which the ore undergoes in such a furnace are rather varied. In the upper parts it is only heated, whereby water is eliminated from hydrated ores, carbon dioxide from iron carbonate, and the ores are converted into ferric oxide or ferroso-ferric oxide. In the lower, hotter parts of the furnace, this is reduced to metallic iron by the carbon monoxide which is present in abundance. Since the temperature is not nearly high enough to melt the iron, the reduced, spongy metal sinks down along with the excess of charcoal to the lowest part of the furnace, where the highest temperature is reached through the combustion of the charcoal in the injected air. The iron here combines with carbon and fuses together, forming cast-iron or crude iron, and collects at the bottom of the furnace.

The iron is run off from time to time and formed into longish blocks, or used for making castings. The slag which is formed at the same time, and which is essentially a mixture of various silicates, floats on the fused iron, and can continually run off through an overflow.

The crude iron obtained in this way contains, besides about 4 per cent of carbon, silicon, phosphorus, sulphur, and also manganese in varying amounts. For the conversion of this into wrought-iron and steel, not only must the amount of carbon be reduced, but the other admixtures, which diminish the value of these other kinds of iron, must be removed as far as possible.

For this purpose, several methods are employed, which differ from one another, however, only in the technical details, but which all amount to the same thing chemically, viz., the removal of the foreign substances by oxidation. The chemical reactions are most readily intelligible in the Bessemer process, which is at present chiefly used.

The iron is introduced in the fused state into a large pear-shaped vessel, and heated air is blown through the molten mass. The impurities then burn more rapidly than the iron, and the products of oxidation pass off in the gaseous state, or pass into the slag which is simultaneously formed. While, in this manner, carbon, silicon, and sulphur can be readily removed, the removal of the phosphorus was not successful as long as there was used for the vessel a lining which consisted essentially of clay. Not until this was replaced by a basic lining consisting of lime or magnesia, whereby the phosphorus passes into the slag as the corresponding phosphate, did it become possible to obtain good wrought-iron or steel from crude iron rich in phosphorus. The slag rich in phosphoric acid which is thereby formed, is used as an important fertiliser in agriculture (p. 523), and is called Thomas's slag, after the inventor of the method.

The course of decarbonisation by the Bessemer process, which takes place in a very short time, can be controlled by spectroscopic observation of the flame produced, and can be interrupted at the desired moment. If 2 per cent of carbon are still left in the iron, steel is formed; if the amount of carbon is reduced to 1 per cent, and less, a kind of wrought-iron is obtained which is called ingot iron.

CHAPTER XXVIII

MANGANESE

General.—The element manganese is very closely related to iron. differs from it in being more readily oxidised, and in its higher co pounds being more readily formed than in the case of iron. For t rest, the corresponding compounds of manganese and iron are ve similar to one another, and in many cases are isomorphous.

In nature, manganese occurs very widely distributed, but is mu less abundant than iron. It is found chiefly as manganese peroxi MnO_2, the many applications of which we have repeatedly noted.

In its chemical relations, manganese is characterised by the ve great diversity of its compounds. It forms not less than five oxidati stages, the lower members of which form bases, the higher, aci There is, accordingly, a correspondingly large number of differe salts containing manganese. By reason of this it exhibits very diver relations of affinity and isomorphism; whereas the lowest series compounds is allied to magnesium, the following ones exhibit is morphism relations with aluminium, titanium, sulphur, and chlorine.

The combining weight of manganese is $Mn = 55{\cdot}0$.

Metallic Manganese.—Pure manganese was formerly litt known. The metal fuses with still greater difficulty than iron, an like the latter, it unites at a high temperature with carbon, so th the element obtained by the reduction of the oxygen compounds wi charcoal always contains a fair quantity of carbon. Manganese fr from carbon can now be readily obtained by reduction with aluminiu according to the method of Goldschmidt, and manganese is thus fou to be a reddish-grey, lustrous metal which is harder than iron a keeps very well in the air, whereas the carbonised metal which w formerly known oxidised very rapidly. It is very readily dissolv by acids, and in this respect probably takes the first place among t heavy metals; even in dilute acetic acid it evolves hydrogen wi great vigour. By the dissolution, the corresponding manganous sa is formed.

Manganese is not used in the free state, but is employed in lar quantities as an addition to iron. White crude iron (p. 564) generally contains larger or smaller amounts of it. Such an iron is especially suitable for being treated by the Bessemer process, as the great heat of oxidation of manganese facilitates the maintenance of the requisite high temperature.

Dimanganion.—The first series of compounds which manganese forms, is derived from the divalent ion $Mn^{\cdot\cdot}$, which, in many respects, has a great similarity to magnesion. Dimanganion has a pale reddish colour, no special physiological action, and its heat of formation is 210 *kj.* All soluble manganous salts are distinguished from the ferrous salts by the fact that they do not oxidise in the air in acid solution.

Manganous Hydroxide, $Mn(OH)_2$, is obtained as a reddish-white precipitate when a solution of a manganous salt is precipitated with alkalis. In the air, this precipitate rapidly becomes brown, hereby passing into manganic hydroxide, $Mn(OH)_3$. It is not disolved by excess of alkalis, but is so by ammonium salts. The reason s exactly the same as in the case of magnesium hydroxide (p. 532); he degree of solubility, also, is about the same. The ammoniacal olution, however, behaves differently in so far as it rapidly becomes rown and turbid in the air. This is due to the absorption of oxygen, vhereby manganic hydroxide is formed, which is much too weak a ase to be soluble in ammonium salts.

By heating the carbonate or by precipitating hot, the anhydride, nanganous oxide, MnO, is obtained in the form of a greenish powder.

Of the manganous salts, the *chloride*, $MnCl_2$, may in the first place e mentioned. It is obtained in the impure state as a residue in the reparation of chlorine from manganese peroxide or pyrolusite (p. 166). t is a pale reddish, easily soluble salt, which crystallises with $4H_2O$.

Manganous Sulphate, $MnSO_4$, crystallises generally in hard, eddish crystals with $4H_2O$; besides this, it can crystallise with $7H_2O$ n the forms of ferrous sulphate, with $5H_2O$ in the forms of copper ulphate, etc. With the alkali sulphates, also, it forms monoclinic louble salts of the type $K_2SO_4 . MnSO_4 . 6H_2O$.

Manganous Carbonate, $MnCO_3$, can be obtained as a reddish recipitate, by precipitating manganous salts with carbonates; it xidises in the air, but much less rapidly than the hydroxide. In ature the carbonate is found as manganese spar; this occurs in hombohedra, which are isomorphous with those of calc-spar.

Manganous Sulphide, MnS, is the most soluble of the sulphur ompounds of the heavy metals which are formed in aqueous solution. t is decomposed even by acetic acid, and can, therefore, not be preipitated from solutions of manganous salts with sulphuretted hydrogen, ut only with alkali sulphides. If the precipitation is carried out in he cold, a slimy, flesh-coloured precipitate (the only sulphur comound of this colour) is obtained; from moderately concentrated solutions in the heat, anhydrous manganous sulphide is sometimes precipitated, under conditions which are not yet exactly known, as a grey-green powder. In the air the sulphur compound oxidises very rapidly, so that it must be washed with a solution of ammonium sulphide when use is made of it for the precipitation of manganese, in analysis.

Manganous Borate is obtained by the precipitation of a manganous salt with borax, and is placed on the market in the form of a brown powder. It is used in large quantities for the preparation of varnish. This is due to its catalytic properties. There are certain vegetable oils, *e.g.* linseed oil, which oxidise in the air to resinous masses. With the crude oils, this oxidation takes place only slowly; if, however, the oil is heated and a small quantity (less than 1 per cent) of manganous borate is added, the absorption of oxygen is greatly accelerated catalytically, and a rapidly drying oil or a varnish is obtained. Further, dimanganion has the property of very greatly increasing the action of certain organic catalysers which accelerate oxidation, the "oxidases."

Manganic Compounds.—The compounds of trivalent manganese or the manganic compounds, are formed from the manganous compounds by oxidation. Even in the case of iron a considerable diminution of the basic properties accompanied the corresponding transformation, a fact which found expression in the incipient hydrolysis of the salts; in the case of manganese, however, the difference is much greater. The hydrolysis of the manganic compounds in aqueous solution is so great that such compounds are quite unstable, and rapidly decompose with separation of manganic hydroxide, $Mn(OH)_3$.

For this reason, very little is known regarding the properties of the ion $Mn^{\cdot\cdot\cdot}$. Its colour appears to be violet-red, and the dark brown colour of some solutions of manganic salts is the result of hydrolysis, since the manganic hydroxide is dark-brown in colour.

The normal hydroxide does not occur in nature, but various anhydrides of it do. The partial anhydride $MnO(OH)$ is called manganite; manganese sesquioxide, or the complete anhydride, Mn_2O_3, is dimorphous, and is called braunite and hausmannite.

In the solid state, some of the manganic salts are known as well-defined compounds. The sulphate is obtained by warming manganese peroxide with concentrated sulphuric acid until it has dissolved to a dark-coloured liquid, and then washing the paste of sulphate, which is formed even in the heat, free from sulphuric acid by means of nitric acid. It is a dark-green powder, which dissolves in water with a violet-red colour, which very speedily changes to brown, manganic hydroxide being deposited. Manganic chloride, $MnCl_3$, is also formed temporarily, when manganic hydroxide is dissolved in cold concentrated hydrochloric acid, and on dilution with water behaves like the sulphate.

Those manganic salts, however, which are not ionised to any great extent, undergo only a slight hydrolysis, as was to be foreseen according to the theory of hydrolysis. To these there belongs, in the first instance, the fluoride, MnF_3, which can be prepared by dissolving manganic hydroxide in aqueous hydrofluoric acid, and which can be obtained in dark-red crystals. This forms double salts with the alkali fluorides, of the type $K_2F_2 . MnF_3 . 2H_2O$.

Finally, the phosphate, $MnPO_4$, appears to be a slightly dissociated salt. It dissolves in excess of phosphoric acid to a red-violet liquid, which is stable even at the temperature of boiling.

Manganese Peroxide.—Tetravalent manganese forms the hydroxide $Mn(OH)_4$, the anhydride of which is the oft-mentioned manganese peroxide, MnO_2. Since even in the case of trivalent manganese the basic properties had practically disappeared, it is natural that tetravalent manganese is no longer capable of forming salts like a base. On the other hand, the acid properties which are present in a pronounced manner in the higher stages of the manganese compounds, begin to be indicated here.

Manganese peroxide occurs fairly abundantly in nature as *pyrolusite*, and is the most important of all the naturally occurring compounds of manganese. It occurs in grey-black crystals, the powder of which is black (not brown).

The hydroxide, $Mn(OH)_4$, is obtained by subjecting manganous salts to strong oxidising actions in neutral or alkaline liquids. As oxidising agent there can be used chlorine, bromine, or a hypochlorite. The hydroxide is dark-brown in colour, and amorphous, and passes readily into the colloidal state. By moderate dehydration, the intermediate anhydride, $MnO(OH)_2$, which has the same appearance, is obtained.

If the hydroxide is treated with cold, concentrated hydrochloric acid, it dissolves with a dark brown-green colour; if the solution is immediately diluted with a large quantity of water, the hydroxide is again deposited. This is due to the formation of a tetrachloride, $MnCl_4$, which is hydrolysed by much water. If the solution is warmed, it becomes colourless and evolves chlorine; manganous chloride remains in the residue. The reaction for the preparation of chlorine given on p. 166 takes place, therefore, in two stages, tetrachloride being first formed and then decomposing into chlorine and dichloride. The equations are $MnO_2 + 4HCl = MnCl_4 + 2H_2O$, and $MnCl_4 = MnCl_2 + Cl_2$.

The manganese perhydroxide prepared as above given, generally yields too little oxygen on analysis. This is due to the fact that the compound, $MnO(OH)_2$ or H_2MnO_3, can act like an acid, corresponding to carbonic acid or sulphurous acid, and form salts. If the manganese peroxide is formed in presence of a base, all the manganese passes into this compound; in the absence, however, of another base, part of the manganese in the divalent state is incorporated in the precipitat the manganous salt of the above acid, *manganous acid*, the formula which is Mn . MnO_3, equal to Mn_2O_3, being formed. If, however, base is present, *e.g.* lime, calcium manganite is formed, and all t manganese passes into the tetravalent state.

* This reaction is made use of for the regeneration of the ma ganese liquors in the manufacture of chlorine from hydrochloric ac and pyrolusite. The requisite amount of lime is added to the liquo in order to convert the manganous chloride into manganous hydroxid and still one combining weight of lime more. If air is blown throug this mixture, oxidation takes place rapidly and readily, and calciu manganite, $CaMnO_3$, is deposited as a black precipitate, known Weldon mud. This again yields chlorine with hydrochloric acid, b half as much hydrochloric acid more is required, as can be seen fro the equation $CaMnO_3 + 6HCl = CaCl_2 + MnCl_2 + Cl_2$.

* At the present day this method is being more and more giv up, as the electrolysis of the alkali chlorides yields more chlorine tha can be made use of in the arts.

Besides being used for the preparation of chlorine, mangane peroxide is employed in pottery works for the production of brow and violet colours. Melts to which manganese peroxide has bee added are coloured violet; if iron is present at the same time, a darl brown colour is produced.

Manganese peroxide is also employed in the manufacture of glas It is there used in order to remove the greenish coloration which th glass assumes owing to the presence of ferrous compounds (p. 528 The action is probably due to an oxidation of the ferrous to the ferri compound, the yellow colour of which is much feebler. Besides thi the yellow colour of the ferric glass is counteracted by the viole colour of the manganese salt, and an imperceptible neutral tint i produced.

* Glass which has been decolorised with manganese exhibits th remarkable property that it slowly becomes red-violet in colour whe exposed to light. This colour passes through the whole mass of th glass, but is absent from those parts where the light was weakened, as for example, behind letters fixed on shop windows. This phenomeno is a proof that in spite of the apparently solid nature of the glass chemical processes can occur in the interior of the mass, as in a liqui which is not in equilibrium.

* Manganese peroxide is also used for making galvanic cells, since it conducts the electric current, and as a cathode gives a fairly hig potential with zinc as anode. The processes taking place in galvanic cells will be discussed in detail at a later point in connection with a simpler case (Chap. XXXII.); at this point it will be sufficient to state that such cells are generally formed of an oxidising agent and a reducing agent, separated from one another by an intermediate con-

ductor, generally a salt solution, and where necessary, a porous partition. On making the proper connection, an electric current is produced whereby the reducing agent is oxidised at the expense of the oxidising agent; the chemical energy which thereby becomes free yields the work necessary for the electric current. In the above cell composed of manganese peroxide and zinc, the manganese peroxide is the oxidising and zinc the reducing agent. Both these are immersed in a solution of sal ammoniac, and when the circuit is closed the zinc dissolves and the manganese peroxide is reduced to manganous oxide.

* Such a cell can be easily made as follows. A mixture of pyrolusite and coke (for the sake of the conduction) is placed at the bottom of a tumbler, a rod of hard, conducting charcoal is introduced into this, and the glass filled with a solution of ammonium chloride; a zinc rod is suspended in the upper part of the liquid in such a way that it does not touch the manganese peroxide and the charcoal (Fig. 112). On uniting the zinc and the charcoal by means of a conductor, an electric current passes through the latter. Such a cell (Leclanché cell) lasts for a long time if only small, intermittent currents are aken from it, as, *e.g.*, for electric ells; for strong, continuous currents t is useless, because the necessary chemical reactions do not occur ufficiently rapidly, and the cell therefore quickly loses its electro-notive force when much used. It recovers its electromotive force on esting.

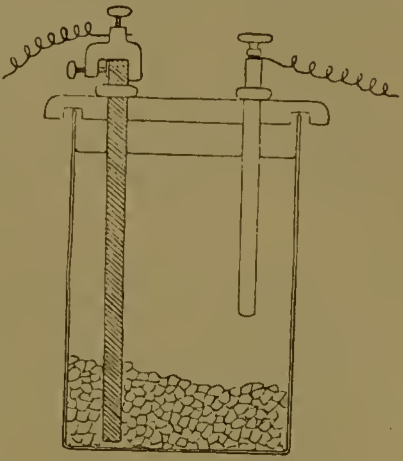

Fig. 112.

On ignition, manganese peroxide loses oxygen, and is converted nto manganoso-manganic oxide, Mn_3O_4, corresponding to ferroso-ferric xide. The reaction is $3MnO_2 = Mn_3O_4 + O_2$. This was formerly the ethod by which oxygen was prepared in the pure state, and it has herefore a certain historical importance.

The same manganoso-manganic oxide, although not of exactly onstant composition, is formed when any of the other oxides of anganese or manganese carbonate is ignited in the air, and this rm is therefore used for weighing manganese in analytical separa- ons. As has been mentioned, however, the composition is not quite nstant; this depends more especially on the temperature, the amount oxygen decreasing somewhat as the temperature rises.

Manganic Acid and Permanganic Acid.—Although com- unds of a pentavalent manganese are not known, manganic acid, $_2MnO_4$, can be regarded as a partial anhydride of the hydroxide of xavalent manganese, for $Mn(OH)_6 - 2H_2O = MnO_2(OH)_2 = H_2MnO_4$.

This interpretation, however, is in the first instance only a formal one, for neither is the hexahydroxide itself nor compounds directly corresponding to it known. It will be found, however, that this interpretation is a convenient one in discussing the oxidation and reduction processes of the manganese compounds.

Manganic acid itself is not known; it is no more possible to prepare it pure than it is to prepare thiosulphuric acid, for its anion cannot exist along with hydrion in solution without at once undergoing transformation. It is known only in its salts, which are stable in alkaline solutions, but in neutral or acid solutions are immediately converted into the ion of the next compound, permanganic acid. The analysis of the salts, and, more directly, the pronounced isomorphism of these with the sulphates, lead to the formula already given, H_2MnO_4.

The salts of manganic acid, or the manganates, are very readily formed by heating any manganese compound with strong bases or with carbonates. If potassium or sodium carbonate (or better, a mixture of these) is heated to fusion and a trace of manganese in any form added to it, the latter dissolves with absorption of oxygen from the air, and imparts a fine dark-green colour to the melt. On cooling, the mass appears almost black when a fair amount of manganese is present, and greenish-blue when only very little is taken. The reaction is so sensitive that it can be used for the detection of manganese. In crude potashes, patches of a blue-green colour are frequently found, due to accidental traces of manganese, which on heating have been converted into manganate.

* In order to prepare potassium manganate, a mixture of pyrolusite and caustic potash is heated in the air; oxygen is thereby absorbed, and a black mass of potassium manganate is formed. When this is dissolved in water a dark green, almost opaque solution is given even with very small amounts.

* The isomorphism with potassium sulphate is seen when this salt is added to the above solution, and this allowed to crystallise. The crystals of potassium sulphate are obtained, coloured in all tints of bright and dark green.

The solution of the crude potassium manganate remains unchanged when it contains a large amount of potash. On adding any acid, the solution acquires a fine red colour, and then contains another compound, which is derived from *heptavalent* manganese. The same colour-change occurs on allowing the dilute solution to stand in the air; the above change is then effected by the carbon dioxide of the air. In passing from green to red, the solution passes through a number of intermediate violet and blue colours, and this change of colour has procured for the substance the name "mineral chameleon."

On adding a fairly large excess of ordinary caustic potash to the solution after it has become red, the colour again changes fairly rapidly to green.

When the red-coloured liquid is evaporated, a salt crystallises out in almost black crystals with a metallic lustre, the composition of which is represented by the formula $KMnO_4$. Apparently, therefore, it contains the same ions as potassium manganate, only in different proportions, there being, in the present case, only one combining weight of potassion to one of the ion MnO_4', instead of two as in the case of the manganates. This, however, furnishes the essential distinction between the two compounds, a distinction which is similar to that between ferrocyanide and ferricyanide. The ions of potassium manganate are $2K^{\cdot}$ and MnO_4''; those of the red salt, which is called *potassium permanganate*, $K^{\cdot}$ and MnO_4'. Whereas, therefore, the former ion is similar to that of divalent sulphuric acid, the composition of the latter is such as to make it more comparable with that of the monovalent perchloranion ClO_4'. As a matter of fact, the two are isomorphous, and if potassium perchlorate is allowed to crystallise in presence of some potassium permanganate, mixed crystals are obtained varying from bright to dark red in colour; this can be seen with especial ease and distinctness under the microscope.

Permanganic acid can be regarded as a partial anhydride of *heptavalent* manganese, for, $Mn(OH)_7 - 3H_2O = HMnO_4$. In agreement with what was set forth on p. 344, permanganic acid has, accordingly, to be regarded as a higher stage of oxidation of manganese than manganic acid, and must therefore be formed from the latter by means of oxidising agents. As a matter of fact, the transformation takes place most smoothly when chlorine is passed into the solution of the manganate, for the following reaction then takes place: $2K_2MnO_4 + Cl_2 = 2KMnO_4 + 2KCl$. The equation of the ions is, $2MnO_4'' + Cl_2 = 2MnO_4' + 2Cl'$. The reaction therefore consists in the transfer of one negative charge from MnO_4'' to the chlorine.

In the transformation of the manganates into permanganates in acid solution, a portion of the mangananion acts as an oxidising agent, he manganic acid being reduced to manganese peroxide.

The reaction may, for example, be written: $3K_2MnO_4 + 4HNO_3 = 2KMnO_4 + 4KNO_3 + MnO_2 + 2H_2O$. It is, however, more instructive o write it so as to show only the reacting ions. We then have $3MnO_4'' + 4H^{\cdot} = 2MnO_4' + MnO_2 + 2H_2O$. This shows that hydrion is used up in the process, and this explains why it takes place in acid olution.

That the reverse transformation from permangananion to mangannion takes place in alkaline solution is to be attributed, on the one hand, to the consumption of hydroxidion, which, of course, takes place more easily in solution containing a large quantity of hydroxyl. The educing action which is at the same time necessary is probably xercised by organic substances, which are generally present dissolved in the caustic potash. Whether, in accordance with the equation $MnO_4' + MnO_2 + 4OH' = 3MnO_4'' + 2H_2O$, permangananion along with manganese peroxide can change into manganauion with consumption of hydroxyl, has not yet been sufficiently investigated.

In contradistinction to manganic acid, permanganic acid is very stable in acid solution. An aqueous solution of permanganic acid can be obtained by decomposing the barium salt in dilute solution with sulphuric acid. A red solution is thus obtained which looks like that of any permanganate whatever, and which conducts electricity like an equivalent solution of hydrochloric acid. Permanganic acid is therefore a strong acid, whose aqueous solutions are largely dissociated even at a moderate dilution.

Of the salts of permanganic acid, the most important is the potassium salt already mentioned, as it is not very readily soluble and crystallises well, and can therefore easily be prepared pure. It is manufactured on the large scale, and in recent times to a large extent by electrolytic oxidation.

Pure permanganic acid, $HMnO_4$, is not known, but its anhydride, Mn_2O_7, is. It is obtained as a brown-green, oily liquid, which separates out in drops by carefully adding concentrated sulphuric acid to dry potassium permanganate; it is very volatile. Even at the ordinary temperature it is converted into a red-violet, readily decomposable vapour which, on slight provocation, decomposes with explosion into oxygen and manganese peroxide, the latter floating around in brown, cobweb-like flakes.

The permanganates are very powerful oxidising agents, and are used as such. Fairly large quantities are used in the chemical industry, especially for the oxidation of organic substances. To the same property is due its application for purposes of disinfection, treatment of wounds, etc.

The mode of action of permangananion in oxidation varies according as it is employed in acid or in alkaline solution. In the former case a manganous salt is formed, in the latter manganese peroxide. Since the latter is a higher stage of oxidation than dimanganion, the oxidation action is more fully taken advantage of in the former case than in the latter.

The oxidising action is so powerful that almost all organic substances are attacked by permanganate. The hydrated manganese peroxide which is thereby formed separates out on the substances and colours them dark brown. On account, therefore, of the resulting decomposition, solutions of permanganates must not be filtered through paper nor kept in contact with indiarubber, cork, or such substances.

* The brown coloration can be readily removed by means of sulphurous acid; soluble manganous sulphate is thereby formed: $MnO_2 + SO_2 = MnSO_4$.[1]

* The same reaction also takes place even in the absence of water:

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[1] In part, also, manganese dithionate is formed: $MnO_2 + 2SO_2 = MnS_2O_6$ (cf. p. 298): the latter is formed chiefly when crystalline peroxide is used, and at a low temperature.

it is therefore made use of in order to remove sulphur dioxide from gas mixtures.

The solutions of the permanganates can all be readily identified by their fine red-violet colour. On examining the transmitted light by means of the prism, five fairly sharp absorption bands are seen lying between the yellow and the green. With equivalent solutions, these bands have exactly the same position and character for all permanganates; they are shown also in exactly the same way by free permanganic acid. This proves that we are dealing here with a definite property of permangananion, MnO_4', which remains independent of the other ion present at the same time in the solution. Since these bands can be measured with great exactness, it has been possible in this case to prove the identity with great strictness.

Potassium permanganate is employed in analytical chemistry. For since its solutions are so strongly coloured that even very small quantities can be recognised, a method for the volumetric determination of reducing agents has been based on the fact that, on oxidising with permanganate, the red colour disappears so long as reducing substance is still present. So soon as this has been used up, even a very slight excess of permanganate can be recognised by the permanence of the red coloration.

This method is chiefly used for the determination of iron, since in acid solution this is immediately converted, even in the cold, from diferrion to triferrion. Since the manganese in passing from permangananion to dimanganion sinks from the heptavalent to the divalent stage, five oxidation units are available. With these, five combining weights of diferrion can be oxidised to triferrion, since for each combining weight only one unit is necessary. If the liquid is imagined acidified with sulphuric acid, the equation, when written in the usual manner, runs: $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$. Omitting the non-essential ions, we obtain the much more simple equation: $5Fe^{\cdot\cdot} + MnO_4' + 8H^{\cdot} = 5Fe^{\cdot\cdot\cdot} + Mn^{\cdot\cdot} + 4H_2O$.

The determination is performed by placing the solution of permanganate in a burette furnished with a glass stop-cock and allowing t to run into the solution of the ferrous salt. Since the method lepends on the oxidation of diferrion to triferrion, all the iron which t is desired to determine must be present as diferrion. In order to btain this, or, as the case may be, to make sure of this, the acid iquid is treated with metallic zinc, whereby any triferrion which may e present is converted into diferrion, a corresponding amount of zinc assing into solution: $2Fe^{\cdot\cdot\cdot} + Zn = 2Fe^{\cdot\cdot} + Zn^{\cdot\cdot}$. The permanganate s then allowed to flow into the solution until the last drop gives a ink coloration to the liquid. The liquid must be maintained fairly trongly acid, as a large amount of hydrion is used up in the reaction. Iydrochloric acid, however, must not be used, since this is partially xidised to chlorine, and too much permanganate is therefore required.

* It is only in the presence of iron that this oxidation of hydrochloric acid takes place in sufficient amount to cause an error in the analysis. If no iron is present, it is possible even to warm dilute solutions of the two substances without appreciable action occurring. We are therefore here dealing with a case of catalytic influence. The presence of dimanganion greatly retards the oxidation of hydrochloric acid by permanganate; if, therefore, for other reasons, iron must be titrated with permanganate in hydrochloric acid solution, it is necessary to previously add an abundance of manganous sulphate.

Besides being used for the determination of iron, permanganate is chiefly employed for the titration of oxalic acid and nitrous acid. The former thereby passes into carbon dioxide, and we have the equation $5C_2O_4'' + 2MnO_4' + 16H^{\cdot} = 10CO_2 + 2Mn^{\cdot\cdot} + 8H_2O$. In this equation, C_2O_4'' is the ion of oxalic acid. If it is desired to write the equation with respect to undissociated oxalic acid, it is only necessary to unite the corresponding $10H^{\cdot}$ with the $5C_2O_4''$, and we obtain $5C_2O_4H_2 + 2MnO_4' + 6H^{\cdot} = 10CO_2 + 2Mn^{\cdot\cdot} + 8H_2O$. In the actual state of affairs, this other method of writing the reaction makes no difference.

This method is used not so much for the determination of oxalic acid (which can be more conveniently determined by means of baryta) as for the estimation of oxalates, *e.g.* calcium oxalate. On account of the great sensitiveness of the reaction, much smaller quantities of calcium oxalate can be determined with permanganate than by weighing; and the method is, therefore, employed where as accurate a determination as possible of very small quantities has to be made.

The volumetric determination of nitrous acid is also carried out in acid solution, and takes place in accordance with the equation $2MnO_4' + 5NO_2' + 6H^{\cdot} = 2Mn^{\cdot\cdot} + 5NO_3' + 3H_2O$. The reaction does not take place instantaneously, and, of course, occurs all the more slowly as the concentration of the nitrous acid decreases during the reaction.

Finally, the use of permanganate for the determination of manganese itself in the form of dimanganion, must be mentioned. When the two ions meet in feebly acid solution, they undergo double decomposition to manganese peroxide, which is deposited as a brown precipitate. If the precipitation is carried out in the heat, the precipitate settles sufficiently quickly, so that the supernatant liquid at once becomes clear, and it can be seen whether it is coloured pink by excess of permanganate. We obtain the equation of the reaction if we consider that all the manganese is converted into the tetravalent form. Each combining weight of dimanganion must therefore take up two units, while the heptavalent manganese of permangananion can give up three units. Two molecules of permangananion, therefore, react with three molecules of dimanganion, and we have $3Mn^{\cdot\cdot} + 2MnO_4' + 4OH' = 5MnO_2 + 2H_2O$.

Hydroxyl is therefore used up in the reaction, and the liquid would become acid if we started with a neutral solution. In strongly acid solution the reaction does not occur. Further, pure manganese peroxide is formed only when a base is present which can combine with it to form a manganite (p. 590). All these conditions are fulfilled if the precipitation is carried out in presence of an excess of zinc oxide.

General Remarks on Oxidising and Reducing Agents.—All oxidising agents can (in the presence of water) be formally regarded as hydroxyl compounds, and all reducing agents as hydrogen compounds of the particular elements. The formulæ of these hydroxides and hydrides are chosen such that they are obtained by the addition of the elements of water to the various substances. In the case of manganese, for example, we have :—

Manganous series	$Mn(OH)_2$	divalent
Manganic series	$Mn(OH)_3$	trivalent
Manganese peroxide	$MnO_2 + 2H_2O = Mn(OH)_4$	tetravalent
Manganate series	$H_2MnO_4 + 2H_2O = Mn(OH)_6$	hexavalent
Permanganate series	$HMnO_4 + 3H_2O = Mn(OH)_7$	heptavalent.

As an example of a series of reducing agents, we choose the compounds of sulphur. Taking sulphuric acid, the hydrogen compound of SO_4, as the initial substance, we have the following formulæ :—

Sulphuric acid	$SO_4 . H_2$
Sulphurous acid	$H_2SO_3 + H_2O = SO_4 . H_4$
Sulphur	$S + 4H_2O = SO_4 . H_8$
Sulphuretted hydrogen	$H_2S + 4H_2O = SO_4 . H_{10}$.

In order, therefore, to oxidise sulphuretted hydrogen, for example, to sulphuric acid, $10 - 2 = 8$ oxidation units must be taken up. If this oxidation is to be carried out in acid solution with permanganate, whereby dimanganion is formed, there are, for each molecule of permanganate, $7 - 2 = 5$ oxidation units available, and since 8 and 5 have no common factor, 5 parts of sulphuretted hydrogen must be used to 8 parts of permanganate.

In order to complete the equation, we must consider that the cations produced, viz., 8 molecules potassion and 8 molecules dimanganion, require together 24 equivalents of anion, of which 5 S yield only 10 as SO_4''. Other 14 equivalents of some acid must therefore be added, *e.g.* $7H_2SO_4$. We therefore obtain the equation $5H_2S + 8KMnO_4 + 7H_2SO_4 = 8MnSO_4 + 4K_2SO_4 + 12H_2O$, or, leaving out the ions which remain unchanged,

$$5H_2S + 8MnO_4' + 14H^{\cdot} = 5SO_4'' + 8Mn^{\cdot\cdot} + 12H_2O.$$

An important point is with regard to the alteration of the acid or basic condition of the reaction mixture in the process, for in general such a change takes place in oxidations, and we have to ask how this s to be calculated. The answer is practically contained in the above examples, still it may be useful to describe the method in detail. It is as follows: Making use only of the elements of water besides the reacting substances, one examines whether after writing the equation obtained from the consideration of the oxidation values, excess of acid or excess of hydroxide appears on the right-hand side. If from this point of view we write the equation for the oxidation of sulphuretted hydrogen with permanganate, we obtain—

$$5H_2S + 8KMnO_4 + 2H_2O = 4K_2SO_4 + MnSO_4 + 7Mn(OH)_2.$$

Besides the neutral salts, therefore, $7Mn(OH)_2$ are formed, *i.e.* 14 equivalents of hydroxyl remain unsaturated, and as many equivalents of an acid must therefore be added in order that the same acid or basic condition may be produced as before the reaction.

The calculation becomes still more simple in the following way. From the practically neutral sulphuretted hydrogen the dibasic sulphuric acid is formed; since $5H_2S$ are oxidised, this corresponds to an increase of the acid by 10 equivalents. On the other hand, 3 equivalents of base are formed from the neutral permanangate, viz., one monovalent potash and one divalent manganous hydroxide. The $8KMnO_4$, therefore, make the reaction mixture more basic to the extent $3 \times 8 = 24$ equivalents. Subtracting the 10 equivalents of acid from this, there remains a basic excess of 14 equivalents, and for these a corresponding amount of acid is necessary in order to maintain the condition unchanged.

In oxidation and reduction processes, therefore, a change in the neutrality, or, more generally, in the acid or basic condition, generally occurs. If hydrion is used up in the reaction, this will, in accordance with the law of mass action, take place all the more readily the more hydrion is present, or the more acid the solution is. The same holds good when hydrion is not used up, but hydroxidion is formed. For since the latter unites with hydrion to form neutral water, the two processes are equivalent in the presence of water. If, on the contrary, hydrion is formed in the process, the latter will take place better in the presence of hydroxidion, and will be retarded or rendered practically impossible by the presence of hydrion. In both cases, indeed, chemical equilibria are established. Very frequently, however, these equilibria are so much towards the one side of the reaction equation that it is not possible to detect the presence of the substances on the other side.

An example of this is afforded by the transformation of mangananion into permangananion, and *vice versa* (p. 593). Since in the case of the direct change hydrion is used up, corresponding to the equation $3MnO_4'' + 4H^{\cdot} = 2MnO_4' + MnO_2 + 2H_2O$, the transformation will be promoted by the presence of hydrion, and the solution will contain permanganate. If the hydrion is decreased by the presence of a large amount of hydroxidion, the mangananion is stable. Another example is afforded by the behaviour of iodine in presence and absence of hydroxidion. Free iodine reacts with hydroxidion to form iodanion and iodidion, in accordance with the equation $3I_2 + 6OH' = 5I' + IO_3' + 3H_2O$. In this reaction much hydroxidion disappears, and the reaction must therefore take place more easily when it is present; as a matter of fact, it takes place in alkaline solution, *e.g.* in a solution of caustic soda. If, however, hydrion is added, the reaction is reversed, and elementary iodine is again set free: $5I' + IO_3' + 6H^{\cdot} = 3I_2 + 3H_2O$.

Complex Compounds of Manganese.—Manganese can form with cyanogen, compounds which are quite similar to those which we have already discussed in detail in the case of iron. In this case also we have the two series of compounds derived from a tetravalent manganocyanidion, $Mn(CN)_6''''$, and a trivalent manganicyanidion, $Mn(CN)_6'''$, and both are obtained in a manner similar to the corresponding iron compounds. They are both, however, less stable, and the manganicyanides, more especially, through their readiness to undergo decomposition, recall the salts of trivalent manganese.

Potassium manganocyanide, $K_4Mn(CN)_6 + 3H_2O$, is isomorphous with potassium ferrocyanide and crystallises in dark blue crystals, which, however, yield an almost colourless solution. Potassium manganicyanide, $K_3Mn(CN)_6$, is red, and is isomorphous with potassium ferricyanide. Its aqueous solutions decompose on being boiled, the manganese being deposited as manganic hydroxide.

CHAPTER XXIX

CHROMIUM

General.—In many of its chemical peculiarities chromium is closely allied to the metals of the iron group, especially to iron and manganese. On the other hand, it is related to the elements molybdenum, tungsten, and uranium, which must be placed in the last group of metals, so that chromium could be grouped just as well with them. It is somewhat arbitrary, therefore, in which group it is placed; that it is here classed in the iron group is done for didactic reasons.

Chromium is closely related to manganese in the number of the series of compounds which it forms. Whereas, however, in the case of manganese, the acids corresponding to the higher stages of oxidation were somewhat unstable, these belong in the case of chromium to the most important and best-known compounds.

Chromium forms the following series of compounds:—

Salts of the divalent dichromion, $Cr^{\cdot\cdot}$.
Salts of the trivalent trichromion, $Cr^{\cdot\cdot\cdot}$, and complex compounds derived from it.
Chromium trioxide, CrO_3, and acids derived from it.
Chromium peroxide, whose composition is not yet known with certainty.

The combining weight of chromium is $Cr = 52{\cdot}1$.

Metallic Chromium was for long known only in the form of an impure product containing carbon, since the fusion of pure chromium could not be effected on account of its high melting point. By the reduction of chromium oxide with aluminium, in accordance with a general method given by H. Goldschmidt, very pure metallic chromium is now manufactured in large quantities. It is used in the iron industry to add to steel (chromium steel).

* This preparation is carried out by mixing chromium oxide with aluminium powder, both carefully dried, and initiating the reaction with a small quantity of the mixture. For this a very high temperature is necessary; this is produced by mixing aluminium powder with

barium peroxide, forming a pill of this, and sticking a piece of magnesium ribbon into it. If the magnesium ribbon is ignited, which can be done with a match, the combustion of the aluminium with the oxygen of the barium peroxide begins; the mass thereby becomes white hot, and initiates the reaction in the neighbouring portions of the chromium mixture. In proportion as this undergoes transformation, more of the mixture is added; the temperature thereby soon rises so high that the chromium fuses.

* The method has the advantage that it does not require a specially built furnace, but can be carried out in an ordinary crucible, preferably one of magnesia; the outside of the crucible becomes only slowly warm. On account of the high temperature of fusion of chromium, the preparation of the fused metal is successful only when fairly large quantities are employed, but then with ease.

* A similar method is used for preparing other metals, and also for the production of very high temperatures. In the latter case cheap oxides, generally iron oxide, are used. With such mixtures fusions, welding, etc., can be carried out on the spot with great ease and certainty, so that the method is of great technical importance.

Chromium is a lustrous white, very hard metal, the melting point of which is about 3000°. Its density is 6·8. It remains unchanged in the air; even at a red heat it becomes only slowly coated with a thin layer of oxide, which exhibits the colours of thin plates. It is dissolved by dilute hydrochloric and sulphuric acids, with evolution of hydrogen. Nitric acid does not attack it, since it becomes "passive" in that acid.

* Chromium passes into this passive state, *i.e.* ceases to be attacked by acids, even by lying in the air. The metal when in this state is not attacked at the ordinary temperature by dilute acids. Treatment of the metal with strong oxidising agents has the same effect. If the passive metal is allowed to lie for a fairly long time under acid, or if this is warmed, dissolution with evolution of hydrogen suddenly commences. If the metal is used as an anode (p. 192) in dilute acid, it is converted by weak currents into its lowest compound, a chromous salt. If, however, the strength of the current is increased, the metal suddenly begins to dissolve in the form of its highest stage of combination as chromic acid. The passive metal likewise becomes active, *i.e.* becomes soluble in acids when it is touched with a piece of zinc or similar metal under acid.

An explanation of these remarkable phenomena, sufficient in all particulars, has not yet been found.

Chromous Compounds.—Dichromion, $Cr^{\cdot\cdot}$, is coloured blue, and has a very pronounced tendency to pass into the trivalent trichromion. It is a very strong reducing agent, and can even decompose water with evolution of hydrogen. The chromous salts can, therefore, be obtained pure only with difficulty, and in aqueous solution cannot be long kept without passing into chromic salts. They are most easily obtained by dissolving metallic chromium in dilute acids; they can also be prepared by the reduction of chromic compounds with metallic zinc. From the solutions bases precipitate chromous hydroxide, $Cr(OH)_2$, as a yellow precipitate, which in the moist state passes into chromic oxide with evolution of hydrogen, and is oxidised almost immediately in the air.

From the solutions of the chromous salts excess of sodium acetate precipitates difficultly soluble chromous acetate, a dark-red, crystalline salt, which can be washed and dried if air is excluded; it is almost the only fairly stable chromous compound. The aqueous solution, prepared with the help of hydrochloric acid, is used for the absorption of free oxygen.

By igniting chromic chloride (*vide infra*) in a current of hydrogen, white, difficultly volatile chromous chloride, $CrCl_2$, which dissolves in water with a blue colour, is obtained.

Chromic Compounds.—Trichromion is violet coloured, and in its properties is most nearly related to aluminion and triferrion, with which it is isomorphous. It has also a highly developed tendency to form complex compounds of all kinds, some of which are violet, some green.

Chromic hydroxide is obtained as a blue-green precipitate by the action of ammonia on solutions of the chromic salts, whereby a small amount of the salt readily passes into complex ammonia compounds. Chromic hydroxide precipitated with alkali hydroxide dissolves in excess of the precipitant to a fine green-coloured liquid, in which the corresponding alkali chromite, *i.e.* a salt of the anion $Cr(OH)_2O''$, is contained. The solution, however, is very unstable; a less hydrated hydroxide of a green colour, which is less soluble than the one directly precipitated, separates out quickly when heated, and slowly in the cold. Such phenomena have already been discussed in the case of beryllium and aluminium.

By partial dehydration various partial anhydrides are obtained from chromic hydroxide. One of these, of the composition $Cr_2O(OH)_4$, is used as a pigment on account of its fine green colour. On ignition chromic oxide, Cr_2O_3, is formed; this can also be obtained in crystalline form by the decomposition of volatile chromium compounds. It then crystallises in the form of corundum (p. 551), and forms black-green, lustrous rhombohedra.

Chromium oxide unites with oxides of divalent metals to form substances of the type of spinel, which are found in regular crystals isomorphous with this substance. Of such compounds by far the most important is chrome ironstone, a compound of chromium oxide with ferrous oxide, $FeCr_2O_4$, which crystallises in black octahedra, and is the compound of chromium most found. Chrome ironstone, therefore, forms the starting substance for the preparation of other chromium compounds.

Of the salts of the chromic series, we must first mention the *chloride*, which is obtained in the anhydrous state by heating chromium oxide and charcoal in a current of chlorine. It sublimes in the form of a fine violet-red (peach-blossom red) substance, consisting of small lustrous scales, which appear to be insoluble in water. On very long contact, however, some passes into solution. The dissolution takes place very quickly, with appreciable rise of temperature, when some chromous chloride is added to the water. Other strong reducing agents have a similar action. A sufficient theory of this acceleration has not yet been given.

From the aqueous solution a green salt with $6H_2O$ is obtained, which cannot be directly converted into the anhydrous chloride, since, like the chlorides of all weak bases, it loses hydrochloric acid on being heated. The green solution is not to be regarded as the (partially hydrolysed) normal chloride with the ions $Cr^{\cdot\cdot\cdot}$ and $3Cl'$, for on adding silver nitrate only $\frac{2}{3}$rds of the chlorine present is precipitated. The last third is therefore not present as ion; the solution also contains free acids. The chloride of a complex divalent cation containing chromium and chlorine, *e.g.* $ClCr^{\cdot\cdot}$, is therefore present. On standing for a lengthened period in dilute solution, the green colour of the solution changes to violet, and at the same time almost all the chlorine can be precipitated by silver nitrate. This corresponds to the formation of the normal chloride, which is accompanied by the production of the violet colour belonging to trichromion. On concentrating and heating the solution the green ion is again chiefly formed. None of these reactions are complete, and to each temperature and concentration there corresponds a definite equilibrium between the two forms. A solution containing almost solely the normal salt is obtained by dissolving the freshly precipitated chromic hydroxide in hydrochloric acid.

The two chlorides can be prepared in the solid state—the normal one by the crystallisation of the solution saturated with hydrogen chloride in the cold, the other in the heat. Both salts contain $6H_2O$; the normal salt is grey-blue, the other is green.

Chromic Sulphate, $Cr_2(SO_4)_3$, exhibits a similar variety of behaviour, and has been still more thoroughly investigated. From aqueous solutions the salt with $9H_2O$ is obtained, and its solutions exhibit the violet colour of the normal trichromion. If the solid salt is heated till it has lost about $3H_2O$, it becomes green, and the solution, immediately after being prepared, exhibits a very small conductivity, and contains therefore scarcely any ions. Its conductivity increases very rapidly; but barium chloride produces no precipitate, which shows that no sulphanion is present. On the contrary, various chromsulphuric acids, or their chromic salts, are formed.

If mixtures of chromic sulphate and sulphuric acid in various proportions are warmed, substances are obtained, the aqueous solutions of which give no reaction with barion, and therefore contain no SO_4''. Neither do they exhibit the reactions of trichromion. They contain complex chromsulphuric acids. The amount of hydrion which they contain corresponds to the hydrion of the sulphuric acid added. In this way as much as $3H_2SO_4$ can be combined with $Cr_2(SO_4)_3$. The solutions are not stable, but soon decompose into their components; the presence of the ions $Cr^{\cdots}$ and SO_4'' can then be detected.

Chromic sulphate forms a regular alum, *chrome alum*, with potassium and ammonium sulphate; this crystallises in very large octahedra of a dark purple colour. If a crystal of chrome alum is suspended in a saturated solution of ordinary alum and crystallisation allowed to take place, the dark octahedron is obtained regularly enclosed in a colourless one. Such regularly zoned crystals are also a sign of isomorphism between the substances which can form them.

Chrome alum is generally prepared by the reduction of potassium bichromate (*vide infra*); it is used in dyeing and for many other purposes. With animal glue the chromic acid, which is split off hydrolytically, forms a compound which is insoluble in hot water; it has a "tanning" action on the glue. Use is frequently made of this property.

Sulphur Compounds of chromium cannot be prepared in the wet way. Sulphuretted hydrogen is without action on chromium salts, and with ammonium sulphide *chromium hydroxide* is precipitated, while sulphuretted hydrogen escapes. That is to say, the hydrolysis of chromium sulphide is so considerable that the compound cannot exist, but decomposes into the substances which are formed from it by the action of water.

At a red heat anhydrous chromium sulphide is formed from the elements in the form of metal-grey, very stable crystals.

Chromic Acids.—When any chromium compound is heated with strong bases or their carbonates, they absorb oxygen from the air and form salts of chromic acid, the anion of which has the composition CrO_4'', and is divalent. The similarity of this formula to that of sulphanion is not only an external one; the two anions are isomorphous, *i.e.* their salts with the same cation have the same form and crystallise with one another in varying proportions.

Chromanion, CrO_4'', is of a pure and strongly yellow colour, and all the solutions of the chromates, therefore, exhibit this colour. The solubility relations of the chromates agree closely with those of the sulphates. Thus, the alkali metals form soluble salts; of the alkaline earth metals, barium forms an extremely difficultly soluble salt, and the others form increasingly more soluble salts. Of the chromates of the heavy metals, that of lead must be called difficultly soluble; this also agrees with what we have in the case of lead sulphate.

Potassium Chromate, K_2CrO_4, is a salt which crystallises in anhydrous rhombic crystals. It is prepared commercially by fusing the naturally occurring chrome ironstone with potashes with access of air. From the aqueous solution it is usual to first prepare the better crystallising potassium dichromate (*vide infra*); from this the normal chromate can be obtained by adding the requisite quantity of potassium hydroxide or potassium carbonate.

Potassium chromate is, at the ordinary temperatures, a sulphur-yellow salt; on being heated it becomes of a bright red colour, but on cooling again assumes its yellow colour. We are here dealing with the shifting of the region in which the salt absorbs the rays of white light with the temperature; the region of the absorption shifting, with rise of temperature, from the violet (which gives the complementary colour yellow, cf. p. 12) towards the green, that is towards the region of longer wave lengths.

The aqueous solution of potassium chromate exhibits an alkaline reaction. This is not due to the chromic acid being a weak acid in the true sense, but is due to the great tendency of the chromates to pass into salts of the condensed dichromic acid, whereby a process similar to hydrolysis is effected. For if any acid, even a weak one, is added to the solution of potassium chromate, a change of colour from yellow to orange occurs, and from the solution another potassium salt crystallises, the composition of which is represented by the formula $K_2Cr_2O_7$. It is therefore the potassium salt of the acid $H_2Cr_2O_7$ which is a *condensed* acid, *i.e.* an acid formed from two combining weights of chromic acid with elimination of one combining weight of water. We have already met with such compounds in the case of sulphurous and sulphuric acids, which were distinguished as "pyro-acids" from the normal ones. The corresponding chromic acid, however, is not called pyrochromic acid but *dichromic acid.*

The transformation of chromanion into dichromanion takes place according to the equation $2CrO_4'' + 2H^{\cdot} = Cr_2O_7'' + H_2O$. For it, therefore, hydrion is necessary, and the reaction accordingly occurs on acidifying the chromates, which contain the ion CrO_4''. In the solutions of the normal chromates the hydrion of the water is used for this purpose; for this reason hydroxidion remains over and the solution reacts alkaline. The hydrolysis which occurs here differs from ordinary hydrolysis (p. 247) in the fact that in this case a condensed ion is formed and not a neutral compound.

For this reason, also, a solution of chromic acid, H_2CrO_4, cannot exist, since, indeed, the hydrion necessary for the transformation is present. When a concentrated solution of potassium dichromate is treated with excess of sulphuric acid, chromium trioxide, CrO_3, the anhydride of chromic and dichromic acid, separates out in long, red, needle-shaped crystals, which are readily soluble in water and exhibit powerful oxidising actions. The aqueous solution of chromium trioxide does not have the bright yellow colour of chromanion but the orange colour of dichromanion, and its behaviour also with regard to the depression of the freezing point and electrical conductivity, allows only of the view that it contains the ions Cr_2O_7'' and $2H^{\cdot}$. If potassium dichromate is mixed with potassium hydroxide, the solution becomes bright yellow and contains potassium chromate. The following reaction occurs: $Cr_2O_7'' + 2OH' = 2CrO_4'' + H_2O$. This is the reverse of the reaction just given, and occurs under the influence of hydroxidion. Dichromanion, therefore, cannot exist in any considerable quantity in presence of hydroxidion, any more than chromanion can in presence of hydrion.

At the present day chromium trioxide is placed at a cheap price on the market, since it is greatly used for galvanic cells and as an oxidising agent in the chemical industry, and since its ready solubility allows of more concentrated solutions of it being prepared than of potassium dichromate, which was formerly employed. Even on being heated it loses a part of its oxygen and passes into chromium oxide. The change takes place more easily in presence of acids, especially sulphuric acid, which form a corresponding chromic salt. This holds good also for the application of chromium trioxide as an oxidising agent. Hydrochloric acid evolves not oxygen but chlorine, being itself oxidised.

Potassium Dichromate is a red-coloured salt which reacts almost neutral; in its solution, therefore, the presence of an acid chromate is not to be assumed. It readily fuses to a dark liquid which on cooling undergoes crystallisation and falls to a powder. It is moderately soluble in water (1 : 10, at room temperature); it crystallises anhydrous.

When potassium dichromate and sulphuric acid are used for oxidation purposes, chrome alum is formed: $K_2Cr_2O_7 + 4H_2SO_4 = 2KCr(SO_4)_2 + 4H_2O + 3O$.

The corresponding sodium salts, *sodium chromate* and *sodium dichromate*, replace the potassium salts at the present time in its applications, since they can be manufactured more cheaply than the latter, by the fusion of chrome ironstone with soda (and lime, to facilitate the reaction). The normal chromate crystallises with $10H_2O$ in the forms and possessing the general solubility relations of Glauber's salt (p. 482); the dichromate crystallises with $2H_2O$.

Of the other chromates, barium chromate may be mentioned. This is obtained as a bright yellow precipitate when the ions $Ba^{\cdot\cdot}$ and CrO_4'' come together in solution. The salt is very stable, withstands a red-heat without decomposition, and is therefore used as a yellow pigment for painting porcelain.

Barium dichromate is not known in the pure form, but its existence in solution can be gathered from the known facts. If the ions $Ba^{\cdot\cdot}$ and Cr_2O_7'' are brought together in solution, barium chromate and not the corresponding salt is formed, and the solution becomes acid. The precipitation is not complete, since, for example, if equivalent quantities of barium chloride and potassium dichromate are used, about a third of the barium remains in solution, and the latter has the orange colour of dichromanion. The cause of this is that in the solution of dichromate, chromanion is also present, being formed in very small amount by the transformation of dichromanion into chromanion through the interaction with water: $Cr_2O_7'' + H_2O = 2CrO_4'' + 2H^{\cdot}$. This reaction is the reversal of that given on p. 605; since it is a case of chemical equilibrium, none of the possible reactions can be complete, but at the end all the substances concerned in the equilibrium must be present. By precipitation as barium chromate the chromanion is removed for the solution, a fresh amount is formed which is also precipitated, and so on. That all the dichromanion does not pass into chromanion is due to the fact that hydrion is produced at the same time, as the above equation shows. The amount of this increases as the reaction proceeds, the stability of the chromanion is thereby diminished, that of the dichromanion is increased, and finally equilibrium must be established. In the solution dichromanion and barion exist side by side without being precipitated, which proves that barium dichromate is a readily soluble compound. The cause of the conversion of dichromanion into chromanion is, therefore, in the present case, the difficult solubility of barium chromate. Since these considerations evidently hold good universally, every cation that forms a difficultly soluble chromate will precipitate this from solutions of the dichromates. This is, as a matter of fact, the case, *e.g.* lead.

The oxidising action of chromic acid can be made use of for its quantitative determination by employing it to liberate iodine from hydrogen iodide, or, in other words, to convert iodidion into iodine. The reaction is

$$Cr_2O_7'' + 14H^{\cdot} + 6I' = 2Cr^{\cdot\cdot\cdot} + 7H_2O + 3I_2,$$

in which 6 equivalents of some anion must be added to both sides in order to make the equation complete. From this it can be seen that a large amount of hydrion is used up in this reaction, which is possible, therefore, only in presence of much acid. For one combining weight of chromium three combining weights of iodine are set free; by means of thiosulphate (p. 488) the amount of the latter can easily be accurately determined.

Sensitive Chromate Mixtures.—Although the chromates alone are not to any great extent sensitive to light, they become so in a very high degree when they are in contact with reducing substances, *e.g.* organic matter like paper, indiarubber, glue, etc. And this sensitiveness is, strange to say, greater in the case of the dry mixtures than when these are moist. On this property a large number of photographic and photo-mechanical methods depend, some of which may be mentioned here.

A mixture of glue and a soluble chromate on exposure to light acquires the property that the glue becomes insoluble. This is due to the fact that the chromic acid is reduced to chromium oxide, which forms an insoluble compound with the glue (p. 604). If some colouring matter is added to the above mixture, and paper is coated with this and exposed to light under a transparent picture, the coating becomes insoluble at those parts on which the light has been able to act, while it remains soluble at the parts where the opaque portions o the picture were. If the prepared paper is treated, after the exposure with warm water, the coating is dissolved at those parts where it was protected from the action of light, while the colour remains at the exposed parts. In order to obtain a picture, therefore, in its proper relations, a "negative" must be used, *i.e.* a transparent picture in which the dark parts are transparent and the bright parts opaque Such pictures are obtained by the ordinary photographic method with silver salts (Chap. XXXV.).

Another method depends on the fact that a mixture of glue and chromate acquires at the exposed parts the property of taking on the oily printing colour, while the non-exposed portions (after the treatment with water) are not coloured by this. If, therefore, the printing colour is rolled over such a picture and a white paper placed on it, a print is obtained in which the exposed parts are again dark and the unexposed bright.

If a metal plate is coated with the chromate-glue mixture, and the part remaining soluble after exposure removed with warm water, the exposed metal can be deeply etched by pouring acid on it. In this way blocks for printing are obtained.

These examples do not exhaust the whole of the possibilities, but we must refrain from further details.

Chromyl Chloride and Chlorochromic Acid.—The similarity of chromic acid to sulphuric acid is further exhibited by the fact that it can form the two chlorides which can be derived from the acid by the replacement of hydroxyl by chlorine.

By distilling a mixture of potassium dichromate and sodium chloride with sulphuric acid, chromyl chloride, CrO_2Cl_2, is formed as a red liquid, similar to bromine, which boils at 118°, and has an appreciable vapour pressure even at the ordinary temperature. As the substance is very sensitive to water, the water formed in the reaction must be bound by using acid containing anhydride, or fuming acid.

Chromyl chloride decomposes, after the manner of the acid chlorides, into chromic acid and hydrogen chloride:

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl.$$

The monochloride of chromic acid corresponding to chlorosulphuric acid is not known, but salts of *chlorochromic acid* are known. The state of affairs is therefore exactly the reverse of that obtaining in the case of sulphuric acid, where the free acid is known but not the salts. Potassium chlorochromate, $KCrO_3Cl$, is obtained as an orange, anhydrous salt by crystallising potassium dichromate from a strong solution of hydrochloric acid: $K_2Cr_2O_7 + 2HCl = 2KCrO_3Cl + H_2O$. On recrystallising from pure water, it again decomposes into hydrochloric acid and potassium dichromate. On being heated it evolves chlorine.

* The formation of chromyl chloride is used for the detection of chloridion in presence of bromidion and iodidion. On distilling the salts in question with potassium dichromate and fuming sulphuric acid, chlorine passes over as chromyl chloride, while bromine and iodine distil over in the free state. The distillate is treated with ammonia, whereby chromyl chloride yields a yellow solution of ammonium chromate, while bromine and iodine dissolve to a colourless solution.

A chromyl fluoride, CrO_2F_2, a red, very volatile liquid, is also known; similarly to the chloride, it is obtained by the distillation of a chromate with fluor-spar and fuming sulphuric acid. It is very rapidly decomposed by water.

Perchromic Acid.—By this name a higher stage of oxidation of chromium is designated, which is formed by the action of hydrogen peroxide on an acid solution of dichromic acid. The solution at once becomes blue; the coloration, however, is not stable, for in a short time oxygen is evolved and a chromic salt is left in the solution. The phenomenon can be made to last longer by shaking out the blue liquid with ether; the blue substance then passes into the ether, in which it keeps much longer.

The composition of this blue compound has, it is true, been determined, but the relations which are met with in this reaction have not been sufficiently explained in order to be treated here.

Since the blue coloration becomes visible with even very small quantities of hydrogen peroxide, an acidified solution of a chromate can be used as a reagent for hydrogen peroxide.

CHAPTER XXX

COBALT AND NICKEL

Cobalt and nickel are two metals allied to iron, and similar to it as far as the compounds of the ferrous series are concerned, but the compounds corresponding to the ferric series are unstable or unknown. These metals, further, share with iron the property of being markedly magnetic, and they also accompany iron in meteorites. Their occurrence in nature is not exactly rare, but they are much more sparingly distributed than iron. They occur chiefly as constituents of complex sulphur and arsenic compounds, and from these they are obtained by first of all being freed from the sulphur and arsenic by roasting, *i.e.* exposure to the oxidising action of the air at a high temperature, whereby they pass into the respective oxides. These oxides are separated from one another in the wet way by the fractional precipitation of the salts prepared from them.

The two elements are grey or yellowish-white metals, the melting point of which is very high, although lower than that of pure iron. They are hard and tenacious metals, which take on a very fine polish; they remain almost unchanged in the air, and have a fairly considerable technical value.

The two elements form divalent, elementary ions; further, they have a great tendency to form complex ions of all kinds. In the case of cobalt, more especially, an extraordinary wealth of different compounds exists, these being chiefly compounds with nitrogen in its various forms of combination, cyanogen, ammonia, and the oxygen compounds.

The combining weights of these elements have been determined by the analysis of their halogen compounds, and have been found to be Co = 59·0, Ni = 58·7.

Metallic Cobalt can be easily obtained as a powder by heating the oxide in a current of hydrogen. In fused masses it is most easily obtained by reduction with aluminium, according to the method of Goldschmidt. It is a tenacious metal, which can be readily polished, and which exhibits a high lustre. In the metallic state it has as yet found no application in the arts.

In most acids it dissolves only very slowly, with evolution of hydrogen, but dissolves readily in nitric acid. The solutions which are formed are coloured red, irrespective of the nature of the acid; it is to be concluded from this that the red colour is due to cobaltion. The cobaltion contained in the salts is divalent, and in its general behaviour is similar to diferrion.

With alkalis, its salts yield a blue-violet precipitate of cobalt hydroxide, $Co(OH)_2$, which is converted into its anhydride, green cobaltous oxide, CoO, on being heated out of contact with oxygen. At a red-heat it takes up oxygen from the air, and an oxide, Co_3O_4, corresponding to magnetic iron ore, is formed, which is again converted into the monoxide at a white heat.

Cobalt hydroxide does not dissolve in excess of alkalis (except in traces, when the solutions are very concentrated), but readily does so in solutions of ammonium salts. The reaction is, in the first instance, similar to that in the case of magnesium hydroxide; but if a large excess of ammonia is added, the red colour changes to a yellow-brown, which shows that a new, complex compound has been formed. If the liquid is diluted with much water, blue cobalt hydroxide separates out as a flocculent precipitate. As in the case of manganese, the ammoniacal solution absorbs oxygen from the air, whereby complex salts are formed which will be mentioned later.

Of the salts of cobalt, cobalt nitrate, $Co(NO_3)_2$, is the best known; it is a readily soluble salt crystallising with $6H_2O$, and is used in analytical chemistry.

Cobalt Chloride, $CoCl_2 . 6H_2O$, is also readily soluble. It forms a large number of lower hydrates, of which the less hydrated forms are of a blue colour. The concentrated aqueous solutions, also, which are red in the cold, exhibit a blue colour when heated. This occurs still more readily when the solution contains a large amount of chloridion in the form of sodium chloride or hydrochloric acid. The cause of this is that under these circumstances the cobaltion is converted into the undissociated salt, the less hydrated forms of which are coloured blue.

* This phenomenon was formerly regarded as a great curiosity, and cobalt chloride was used as a "sympathetic ink." For, on writing on paper with a solution of this salt, the pale-red tracings are scarcely recognisable in the ordinary state. On heating the paper, however, and thereby converting the salt into the less hydrated form, the blue olour appears very distinctly.

* Textile material moistened with a concentrated solution of the alt, assumes various colours when exposed to the air, according to he amount of moisture in the latter. In dry air it is blue; in moist, pale red; in the intermediate states, violet colours appear. uch material is used as a rough hygroscope, because, from its colour, an idea can be obtained as to the amount of moisture in the air and he probability of rain.

* These properties do not belong exclusively to the chloride of cobalt; they are also more or less markedly exhibited by the other salts. The anhydrous salts of cobalt are all coloured blue.

Cobalt sulphate, $CoSO_4 . 7H_2O$, usually crystallises in the forms of ferrous sulphate; as in the case of the other vitriols, salts of various forms, sometimes also with different amounts of water of crystallisation, are obtained, according to the temperature. With potassium and ammonium sulphate, monoclinic double salts with $6H_2O$, of the type which has already been mentioned several times, are formed.

Cobalt Silicates.—When glass is fused with cobalt compounds, dark blue fusions are obtained, the colour of which is due to cobalt silicate. Even in comparatively small amount, this substance imparts a blue coloration to glass (as also to the borax and metaphosphate bead); the transmitted light is found to be composed of blue together with violet and red, while the intermediate rays (orange, yellow, and green) are very completely absorbed. To this property is due the use of cobalt glass for the detection of the potassium flame in presence of that of sodium.

In the arts, use is made of the above property for the production of blue glass, and also of blue pigments for porcelain, as well as of other blue colours. The finely powdered cobalt glass is used as a pigment under the name of smalt or "cobalt," and is distinguished by its very great resistance to chemical influences. As a pigment for porcelain, more or less pure cobaltoso-cobaltic oxide is generally used, which passes into cobalt silicate with the silicates of the glaze. Over most of the other colours, this one has the advantage that it withstands the high temperature of the porcelain furnace, and can therefore be painted on under the glaze, whereas the less stable colours must be burned on the glaze at a gentle heat after the object has been made, and are therefore not so durable.

Cobalt Sulphide, CoS, is obtained as a black precipitate on adding ammonium sulphide to solutions of cobalt salts; the precipitate is also produced on passing sulphuretted hydrogen into a solution of a cobalt salt to which excess of sodium acetate has been added. If the solution is strongly acid, *i.e.* if it contains hydrion in considerable concentration, no precipitate is produced.

While other sulphides, however, which have similar solubility relations, readily re-dissolve in dilute solutions of strong acids (cf. zinc), cobalt sulphide when once formed is found to be insoluble in acids. The explanation of this remarkable phenomenon is probably this, that the precipitate, after being formed, at once undergoes a change o state, whereby it becomes less soluble. This behaviour can be wel made use of for analytical purposes, since in this way cobalt and nicke (which has a similar behaviour) can be separated from the metalli sulphides, which do not exhibit the above peculiarity.

Other Cobalt Compounds.—On igniting any cobalt salt with excess of alumina, a fine blue-coloured, unfused mass is produced, which is also used as a pigment. This reaction is made use of for the detection of alumina with the blow-pipe. With zinc oxide a mass of a strong green colour is produced.

A higher oxide of cobalt, Co_2O_3, corresponding to ferric oxide, is obtained by gently igniting cobalt nitrate; the corresponding hydroxide is obtained by the action of strong oxidising agents, such as sodium hypochlorite, on cobaltous hydroxide. This hydroxide, however, forms no stable salts, although solutions of cobaltic salts, among others, are obtained on subjecting cobaltous salts to the oxidising action of an electric current at an anode of platinum. These salts are distinguished by a fine dark-green colour, but undergo hydrolytic dissociation to a large extent.

Complex Salts of Cobalt.—From cobalt, two series of cyanogen compounds are in the first instance derived, corresponding to the two series of iron-cyanogen compounds. Thus, there is a tetravalent cobaltocyanidion, $Co(CN)_6''''$, and a trivalent cobalticyanidion, $Co(CN)_6'''$, and derivatives of these. Of the two, the second is by far the more stable.

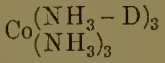
From cobaltous salt and potassium cyanide a red solution is produced in the cold, and, by special precautions, a violet salt can be obtained from this similar to potassium ferrocyanide. On being heated, the solution becomes colourless, passing into the cobaltic compound with decomposition of the water and evolution of hydrogen, and on evaporation the colourless, very stable potassium cobalticyanide, $K_3Co(CN)_6$, is obtained; from this the hydrocobalticyanic acid, $H_3Co(CN)_6$, which is also exceedingly stable, can be obtained in the form of colourless, acid, readily soluble needles.

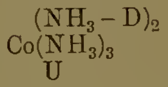
Another complex salt, the formula of which has a certain similarity to the one just described, is obtained by mixing a solution of a cobalt salt with potassium nitrite and adding acetic acid. The red colour of the solution disappears and gives place to a yellow; after some time all the cobalt is then present in the form of a yellow, crystalline salt, which is deposited as a heavy powder. The salt is very difficultly soluble in its mother liquor, so that very small amounts of cobalt can in this way be precipitated and detected. The reaction is of especial value from the fact that it is not given by nickel, although in almost all other reactions the latter agrees with cobalt.

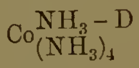
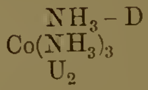
The salt is found, by analysis, to have the composition $K_3Co(NO_2)_6$; it is the potassium salt of the trivalent cobaltinitrosion, $Co(NO_2)_6'''$. This salt is distinguished from the analogously constituted cobalticyanidion by its much smaller degree of stability, for it is not known as an acid, but only in its normal salts.

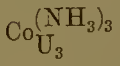
Cobalt-ammonia Compounds.—When excess of ammonia is added to cobalt salts and the solutions which are formed exposed to the action of oxidising agents, *e.g.* of the atmospheric oxygen, very varied compounds are produced, the empirical composition of which is one combining weight of cobalt salt plus three to six combining weights of ammonia. Expressed in formulæ, therefore, the composition of the chlorides, for example, would be $CoCl_2 . nNH_3$, where n is equal to 3, 4, 5, or 6. These salts, however, do not behave at all like cobalt salts, for they are mostly very stable and do not give the ordinary reactions of cobalt, but special reactions which differ essentially in the different series; they are, therefore, salts of new cations consisting of cobalt and the elements of ammonia. They could, then, in the first instance, be regarded as compounds of new, trivalent cations, having the composition $Co(NH_3)_n^{\cdots}$. In opposition to this, however, is the fact that the *anions*, also, which are contained in the salts, do not always exhibit the reactions of these ions, so that the further conclusion must be drawn that the elements of the anions are also partially contained in the complex cation.

The following rule affords a survey of the various compounds which exist here. The cobalt in these compounds is regarded as *nonavalent* and the ammonia as divalent. The compounds can then be so formulated that the non-ionisable anions are united *directly* with the nonavalent cobalt, while the ionisable anions appear *indirectly* united with the cobalt by means of the ammonia. To this the empirical rule has to be added that there are never more than three equivalents of anion united (directly or indirectly) with one mole of cobalt. From this we obtain the following possibilities :—

Trivalent . . .  $\mathrm{Co}\genfrac{}{}{0pt}{}{(NH_3-D)_3}{(NH_3)_3}$

Divalent . . .  $\overset{(NH_3-D)_2}{\underset{U}{\mathrm{Co}(NH_3)_3}}$

Monovalent . . .  $\mathrm{Co}\genfrac{}{}{0pt}{}{NH_3-D}{(NH_3)_4}$ and  $\overset{NH_3-D}{\underset{U_2}{\mathrm{Co}(NH_3)_3}}$

Avalent . . .  $\mathrm{Co}\genfrac{}{}{0pt}{}{(NH_3)_3}{U_3}$

For the purpose of better distinguishing the ionisable anions from the non-ionisable, the former are denoted by D, the latter by U.

The above cases become still more diverse from the fact that not only can the most varied anions be present, but the place of ammonia can be taken by other substances, *e.g.* by water, and also by numerous organic compounds.

Moreover, the anions directly united with cobalt are not completely bound, but, in their turn, also undergo a greater or less dissociation, according to their nature, and although this dissociation is generally much less than that of the other ions, it is by no means to be always neglected.

A description of these numerous compounds will not be undertaken here, especially as many problems regarding their nature still remain unsolved. We shall merely state generally that the complex cations of these salts are almost all more or less brightly coloured; the old designation of these salts, indeed, is derived from their colorations. The "luteocobaltic" salts are the compounds of the first type, the purpureo-salts belong to the second, the praseo-, flaveo- and croceo-salts to the third type. The complex cations mostly form strong bases with hydroxyl, which are soluble in water and exhibit the reactions of hydroxidion in a most pronounced manner. Their salts are frequently very difficultly soluble in water.

Nickel.—Unlike cobalt, which is not employed in the metallic state, metallic nickel is a material which is greatly used. It was formerly used only for alloys; thus German silver is an alloy of nickel with zinc and copper. Some decades ago, however, the difficulties caused by the high temperature of fusion of nickel have been overcome (especially since it was found that it could be rendered more easily fusible by the addition of metallic magnesium or aluminium), and at the present day nickel is extensively employed in cases where it is required to use a tenacious and hard metal, and one which keeps well in the air and is difficultly fusible. It finds increasing use, therefore, for apparatus in the laboratory and for household utensils.

Further, large quantities of nickel are deposited on other metals with the help of the electric current. It coats these with a resistant, almost silver-white layer, which keeps well in moist air, so that the *nickel-plating* of various objects made of iron and brass has become an extensive industry.

* The electrical deposition of a metal depends on the fact that at the cathode of a circuit, the cations pass from the state of ions into the neutral state. In the case of nickelion, this passes into metallic nickel, which is deposited at all points where the current leaves the liquid. In this process various circumstances, such as strength of the current, nature of the solution, etc., have a considerable influence on whether the metal is deposited in a coherent, lustrous layer or as an incoherent powder. The practice of *electro-plating*, as this process is called, depends on the knowledge and application of the conditions which ensure the formation of a good deposit. This subject, which is very important in the arts, has been only very little investigated scientifically, so that no general rules can be given.

* In order that the nickel-plating bath, which constantly gives up metal to the object to be plated, may not become exhausted, the anode is made of metallic nickel. By this means the anion is not discharged, but on the contrary, as much neutral or metallic nickel passes into the ionic state as is separated at the cathode, and the whole process consists in metal passing into ions at the anode, and being transported by the current to the cathode, where it again passes from the ionic state

into the metallic. In this process the current would, theoretically, have practically no work to perform; as a matter of fact, however, a larger or smaller amount of work must be performed by the current on account of the differences in the concentration and other circumstances, a fact which finds expression in the so-called *polarisation* of the bath or the "bath potential."

Nickel forms a divalent elementary ion, nickelion, $Ni^{\cdot\cdot}$, which is of a fine green colour; this colour is present in all solutions of nickel salts which contain this ion. Nickel, it is true, can also form a higher stage of oxidation, but this is extremely unstable, and does not behave as a salt-forming oxide. Nickel can form complex ions, but these are neither so varied nor so stable as in the case of cobalt; this forms the most essential difference between the otherwise very similar elements.

Nickel salts are obtained by the dissolution of metallic nickel in nitric acid; in the case of nickel, the decomposition of aqueous acid solutions with evolution of hydrogen takes place only very feebly and slowly. If *aqua regia* is employed, the chloride is obtained; by evaporating the nitrate with sulphuric acid, the former is converted into the sulphate.

From the green solutions of the nickel salts, soluble bases give a pale green precipitate of *nickel hydroxide*, $Ni(OH)_2$, which loses water when heated, and is converted into grey *nickel oxide*, NiO. Nickel hydroxide is not soluble in alkalis, but dissolves in ammonia. As the liquid thereby becomes of an azure blue colour, it must be concluded that a new ion is formed. The investigation of the solid salts has shown that we are possibly dealing with two different ions, one of which contains $4NH_3$, the other $6NH_3$, to one Ni; the ions, therefore, have the formulæ $Ni(NH_3)_4^{\cdot\cdot}$ and $Ni(NH_3)_6^{\cdot\cdot}$. They are both blue.

* The complex ions of nickel containing ammonia differ from those of cobalt, not only in being derived from divalent nickel, but also in being much less stable. Whereas most of the cobalt-ammonia compounds can be brought together with bases, and even in some cases boiled with them, without ammonia being eliminated to any appreciable extent, the salts of the nickel-ammonia ions in the solid state slowly lose their ammonia even in the air, and quickly on heating. The dissociation pressure of these compounds therefore in respect of the ammonia has an appreciable value even at the ordinary temperature, while in the case of the cobalt compounds it is immeasurably small.

The nickel salts are similar to those of cobalt and generally isomorphous with them. Of these salts some importance is possessed by *nickel sulphate*, which is generally obtained in quadratic crystals with $6H_2O$, a form which is seldom found in the case of the other vitriols; it can, however, also crystallise in the forms of magnesium sulphate and ferrous sulphate. With potassium and ammonium sulphate, it forms double salts of the oft-mentioned type. Nickel sulphate and a double salt with ammonium sulphate are used in large quantities for the preparation of baths for nickel-plating.

With potassium cyanide, the nickel salts at first deposit a green precipitate of nickelous cyanide, which dissolves in excess of potassium cyanide and yields a yellow liquid. From this change of colour it can be seen that a new ion is produced; on evaporating the solution a yellow salt of the composition $K_2Ni(CN)_4 . H_2O$ crystallises out. The nickel cyanidion which forms the basis of this salt does not have an analogous composition to the complex ions of iron, manganese, and cobalt, for it is only divalent. With regard to its stability, also, it differs greatly from these compounds. On acidifying the solution one does not obtain free hydronickelcyanic acid, but a greenish precipitate of nickelous cyanide is produced and hydrocyanic acid escapes. The acid, therefore, immediately decomposes according to the equation $H_2Ni(CN)_4 = Ni(CN)_2 + 2HCN$. A separation of cobalt and nickel can be based on this reaction.

Nickel Carbonyl.—If carbon monoxide is kept in contact with finely divided nickel at a temperature of about 30°, the two substances combine to form a colourless liquid which boils at as low as 43°, and has an unpleasant smell and poisonous action. The composition and vapour density are represented by the formula $Ni(CO)_4$.

The liquid is not appreciably soluble in water, but it readily dissolves in organic liquids, such as benzene and turpentine. In the air it oxidises to substances of complex composition.

At a somewhat higher temperature, nickel carbonyl again decomposes into its constituents; for each temperature there exists a relation between the carbon monoxide and the vaporous nickel carbonyl at which equilibrium exists with metallic nickel: with rising temperature the equilibrium shifts in favour of the carbon monoxide.

By reason of this, nickel can be separated in the pure state from its ores after it has been reduced to spongy metal at a low temperature. Carbon monoxide is passed over it, and the resulting gas mixture is heated; metallic nickel is thereby deposited and the liberated carbon monoxide can be used for the conversion of fresh quantities of nickel. For technical purposes, however, this process cannot be employed, because, under the above conditions, the carbon monoxide also undergoes decomposition into carbon and carbon dioxide, $2CO = C + CO_2$, which disturbs the cycle of processes.

* The change of equilibrium with rise of temperature brings it about that metallic nickel can be distilled from a lower to a higher temperature. Carbon monoxide is enclosed in a glass tube, at one end of which there is nickel sponge, and the end at which the nickel is not placed is heated to 100° or somewhat over this. After a short time the hot end becomes covered with a fine mirror of metallic nickel.

CHAPTER XXXI

ZINC AND CADMIUM

Zinc.—From the metals of the iron group, to which it is in many respects similar, zinc differs in the fact that it cannot form any other stage of combination than that containing divalent ion. In this respect it forms an intermediate member between nickel, which has lost this property almost entirely, and magnesium, in the case of which no trace of that property is present.

Zinc occurs fairly abundantly in nature, both as oxygen compounds (carbonate and silicate), and as sulphide or *blende*. Zinc is obtained from both these and is a white, fairly soft metal which melts as low as 420° and boils at 950°. In the air and in water it oxidises very quickly. Since, however, the zinc hydroxide or carbonate which is formed covers the underlying metal with a coherent coating, the oxidation proceeds for the most part slowly, and objects made of zinc resist the influences of air and water fairly well.

Cast zinc is coarsely crystalline and brittle. If, however, the metal is heated to somewhat over 100°, it becomes soft and tenacious, and can be hammered and rolled. Having once undergone this treatment, it remains tenacious even at the ordinary temperature. If it is heated to about 300°, it again becomes extremely brittle, and at that temperature can be ground to a powder; on being cooled, it retains a somewhat brittle character.

Zinc is employed not only in the pure state, but also to a large extent in alloys. Its most important alloy is that with copper: it is called brass, and will be treated under copper. With copper and nickel it forms German silver (p. 615).

Zinc is also used for coating iron in order to protect it from rust: this is then known as "galvanised" iron. Iron objects which remain constantly exposed to the air, such as railings, agricultural implements, etc., are in this way rendered durable. It is true that zinc in contact with iron oxidises more quickly than when alone, but the oxidation is limited to the surface.

At 420° zinc fuses, and this temperature is low enough to allow of the metal being largely used for castings. At 950° zinc is converted into a vapour, which burns in the air with a brilliant blue flame, forming zinc oxide. The density of this vapour yields the molar weight 65·4; as this number also represents the combining weight, the formula of zinc in the vaporous state is Zn. It contains, therefore, only one combining weight, whereas most of the elements in the gaseous or vaporous form have the double formula. The other metals, however, so far as they are known in the vaporous state, exhibit the same peculiarity as zinc.

It is on the volatility of zinc that its manufacture depends. The oxygen ores are heated directly with charcoal; the sulphide, after being converted into zinc oxide by roasting in the air. The metal formed by the reduction of the oxide with charcoal volatilises and is collected in suitable receivers with exclusion of air, while the impurities remain behind in the retort.

In this process a portion of the metal is obtained in a form in which it is often used in the laboratory, viz. as *zinc dust.* So long as the temperature of the receiver remains below the melting point of zinc, the metal is deposited in the form of a fine grey powder. (The relations are exactly the same as in the formation of flowers of sulphur.) This powdery form of zinc is more suitable for many chemical purposes than the fused; in using it, however, it must be remembered that it generally contains a considerable amount of zinc oxide in consequence of an incipient oxidation.

Recently many attempts have been made to obtain zinc from its ores by first converting it into a salt and then decomposing this by means of the electric current. The difficulty of obtaining a coherent metal free from oxide in this way does not appear as yet to have been overcome.

Zincion.—Metallic zinc readily dissolves in acids with evolution of hydrogen (p. 85), and is converted into the corresponding zinc salt, *zincion*, $Zn^{\cdot\cdot}$, being formed from the metal.

Zincion is divalent, and resembles magnesion in many respects. Like the latter it is colourless, and with the different anions it forms salts which have similar solubilities and the same crystalline forms as the magnesium salts. Zincion is a poison for the higher organisms; nevertheless, it has been found as a constituent of some plants which grow in soil containing zinc.

The heat of formation of zincion from the metal is 147 *kj.* This is, therefore, also the amount of heat developed by the dissolution of zinc in acids (p. 201).

* During the dissolution some remarkable peculiarities are observed. Pure zinc appears as almost insoluble in dilute acids. So soon, however, as there is added a small quantity of a salt of copper, silver, lead, or some other metal, which is eliminated from its solutions by zinc, a rapid evolution of hydrogen at once occurs. The cause of this is at once seen on touching a piece of zinc immersed in an acid with a piece

of another metal. Hydrogen is abundantly evolved, but only at the surface of the other metal, while the zinc passes quietly into solution. If different metals are used as cathodes for an electrical current in dilute acid, it is seen that for the evolution of hydrogen at a surface of zinc a much higher potential is required than in the case of any other metal.

* The process may therefore be pictured as if the zinc withdrew the charge from the hydrion, passing thereby into zincion, while the hydrogen assumes the gaseous form. This passage into the gaseous state takes place (for reasons which are not yet known, but which are detected by the potential) with much greater difficulty at a surface of zinc than at the surface of another metal, and for this reason the decomposition is slight so long as only zinc surfaces are available for the evolution of gas. If, however, the zinc is connected by a conductor with another metal at the surface of which the hydrogen can be more readily evolved, the formation of the zincion and the elimination of the hydrogen take place at different points, an electric current passing at the same time through the metals and the acid. In Fig. 113 a clear picture of these relations is given. From the zinc, denoted by Zn, the metal dissolves as ion; the requisite amounts of positive electricity are withdrawn from the hydrion present in the solution, these charges passing in the direction of the arrows through the metallic conductor to the zinc. The simultaneous production of an electric current is, therefore, the necessary condition for the dissolution of zinc and the evolution of hydrogen occurring at two different points.

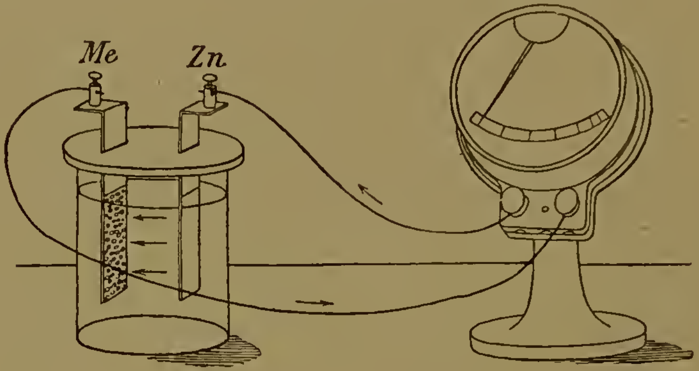


Fig. 113.

* The above arrangement affords at the same time an insight into the production of electric currents in the old voltaic cell, consisting of zinc, copper, and dilute acid. Fuller information on this point will be given at a later point (Chap. XXXII.).

Zinc Hydroxide, $Zn(OH)_2$, is deposited as a white, flocculent precipitate on the addition of dissolved bases to a solution containing zincion. It is soluble in an excess both of alkali and of ammonia, although for different reasons in the two cases. The solubility in alkali depends on its property of splitting off hydrion from its hydroxyl, and therefore of acting as an acid. These solutions contain an alkali *zincate, e.g.* K_2ZnO_2, and the new ions ZnO_2'' and $HZnO_2'$. The reason of the solubility is therefore the same as in the case of alumina (p. 551). The solubility of zinc hydroxide in ammonia, however, depends on other causes. We might regard it as being due to an influence exerted on the solubility by the presence of ammonion, such as occurs in the case of the otherwise very similar magnesia (p. 532). This appears, however, to be excluded from the fact that zinc hydroxide must be a much weaker base, as is evident from its solubility in alkalis (p. 551). On the contrary, we have here to assume the formation of new zincammonium ions, $Zn(NH_3)_n^{\cdot\cdot}$, where n has presumably several values. The behaviour of zinc hydroxide is therefore comparable with that of nickel hydroxide, in which case the formation of new ions was rendered visible by the change of colour.

* This assumption is supported by the fact that the zinc salts, especially the halogen compounds, even when dry, readily combine with ammonia without undergoing decomposition.

On being heated, zinc hydroxide loses water, and is converted into white *zinc oxide*, ZnO. The same compound is obtained by heating metallic zinc in the air; in this way it is prepared on the large scale for use as a pigment under the name *zinc white.*

Over white lead, which is employed for similar purposes, zinc white has the advantage of being less poisonous, and of remaining white even in an atmosphere containing sulphuretted hydrogen, whereas the former becomes dark in colour. White-lead, however, has a better covering power, since it has a considerably higher coefficient of refraction than zinc white, and for this reason it is still often preferred.

* The use of colourless substances, as white paints, depends on the fact that in the small particles of which the paint consists the light undergoes repeated refraction, and is ultimately totally reflected. This total reflection effects the "covering" power, *i.e.* the opacity of the layer. Of the variously directed rays in an opaque body, the number of those which are totally reflected is all the greater, the greater the index of refraction, because the angle at which the light rays can still pass through decreases in the same proportion. Hence proportionately thin layers suffice in order to reflect all the incident light.

Zinc oxide is white in the cold, but appears yellow when hot; on cooling it again acquires a white colour. This colour change must not be regarded as a sign of the conversion of the zinc oxide into another, perhaps allotropic, condition, for it does not take place suddenly, as in such a case it would do, but gradually. It is solely due to the fact that the region in which zinc oxide absorbs rays moves, on heating, from the ultra-violet portion of the spectrum, in which it is situated at the ordinary temperature, towards the visible violet portion. This is a very general phenomenon, viz. that the region of absorption of rays changes in the above sense with the temperature. White substances become yellow on being heated, yellow ones red (p. 605), and red ones brown; blue and green substances, on the other hand, generally undergo no marked change of colour on heating.

Zinc Chloride, $ZnCl_2$, is a white, readily soluble salt, which boils as low as 730°, and can be easily obtained in the dry or wet way by the action of hydrochloric acid on zinc or zinc oxide. On being evaporated to dryness, the aqueous solution loses hydrochloric acid. The product can be again freed from oxygen by distillation in a current of hydrogen chloride or by the electrolysis of the fused salt, the spongy zinc which separates out acting as a purifying agent. Zinc chloride melts very readily to a clear, strongly refracting liquid.

Zinc chloride is used as a preventative of the destruction of wood by micro-organisms and fungi, *e.g.* in the case of railway sleepers. Further, it is used as a flux for soft solder. In this case its action is due to its power of dissolving metallic oxides (p. 429).

A concentrated solution of zinc chloride dissolves large quantities of zinc oxide. From the solution an oxychloride, $\mathrm{Zn}\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{Cl}}$, crystallises out. If the solution is very concentrated, the whole solidifies to a hard mass of oxychloride. This phenomenon is made use of for the preparation of a cement, a solution of zinc chloride of syrupy consistency being rubbed together with zinc oxide shortly before it is required for use.

On diluting the solution containing the oxychloride with water that substance (or, in the case of very dilute solutions, zinc hydroxide) is precipitated. Since almost all commercial zinc chloride contains oxychloride, *i.e.* has lost hydrogen chloride on evaporation to dryness, the same phenomenon is there met with, the salt yielding a turbid solution, or, on dilution, depositing a white precipitate.

The formation of a basic precipitate is also promoted by the hydrolytic decomposition of the zinc chloride in the solution. On account of the feebly basic properties of the hydroxide, this decomposition is rather considerable, and manifests itself in the acid reaction exhibited by the solutions of all zinc salts.

Zinc Sulphate, or zinc vitriol, $ZnSO_4$, generally crystallises with $7H_2O$ in the rhombic forms of magnesium sulphate. According to the temperature, however, it can crystallise with other amounts of water, and in other forms. It is a colourless salt, very readily soluble in water, and can be obtained by the action of sulphuric acid on zinc oxide or metallic zinc; it is employed in the arts and in medicine. It forms, with the sulphates of potassium and ammonium, double salts containing $6H_2O$.

Zinc Carbonate, $ZnCO_3$, occurs naturally as calamine, and is a highly valued zinc ore. It crystallises in rhombohedra, which are isomorphous with those of calc-spar. As in the case of magnesia, basic carbonates, varying with the temperature and the dilution, are mostly obtained by precipitating aqueous solutions of zinc salts with alkali carbonates. They are converted into zinc oxide by ignition. Precipitation as carbonate, and weighing as oxide, are used for the analytical determination of zinc.

Zinc Silicate also occurs naturally as siliceous calamine. It is also used in the manufacture of zinc.

Zinc Sulphide, ZnS, is obtained as a white, hydrated precipitate by the addition of ammonium sulphide to zinc salts. Of the better known heavy metals zinc is the only one which forms a white sulphide; this serves as a convenient characteristic in analysis. Zinc sulphide is soluble in dilute acids with liberation of sulphuretted hydrogen. The reaction takes place in a manner similar to that in the case of iron sulphide (p. 577), but with the difference that zinc sulphide is considerably less soluble. This is the reason that a neutral solution of zinc sulphate or zinc chloride is precipitated by sulphuretted hydrogen; not until a pretty considerable portion of the salt has undergone double decomposition does the concentration of the hydrion produced reach such a value as to hinder further precipitation. If the concentration of the hydrion is raised to this value to start with, by the addition of hydrochloric or sulphuric acid, no precipitation is produced by sulphuretted hydrogen. For equilibrium depends only on the relative concentrations existing in the solution, and not on the amount of the solid substances.

If, however, by suitable means the concentration of the hydrion is kept so low that the state of equilibrium is not reached, the zinc can be almost completely precipitated from acid solutions. As has been mentioned several times, this is brought about by the addition of an acetate. The acetanion present then withdraws the hydrion produced in order to form undissociated acetic acid, and only a very small portion of the hydrion escapes this combination.

* If in this manner zinc is precipitated from acetic acid solution in presence of cobalt and nickel, white zinc sulphide is first deposited, and black cobalt sulphide and nickel sulphide do not make their appearance till later. In this way the presence of zinc along with those other metals can be detected in analysis.

In nature, zinc sulphide occurs in brown to black masses, and is called *zinc blende,* or simply blende. It is an important zinc ore. The sulphur is removed by roasting, and the oxide formed is reduced with charcoal. The process which occurs in the roasting is represented by the equation $2ZnS + 3O_2 = 2ZnO + 2SO_2$. The sulphur dioxide thereby produced is used for the preparation of sulphuric acid. This is done not only for the sake of utilising it, but also in order that it may not escape into the air and exert its destructive action on plant growth.

Cadmium.—This element, which is very similar to zinc, occurs in comparatively small amount in nature, associated with that metal. A it is more readily volatile than zinc, it collects in the first portions o the distillate in the preparation of the latter. It is a bluish-whit metal, almost as soft as lead; it melts at 320° and boils at 770° Its vapour density points to a molar weight, which is equal to th combining weight, Cd = 112; the formula of the element in the vaporou state is therefore Cd, similarly to zinc.

Cadmium forms only one elementary ion, divalent cadmion, $Cd^{\cdot\cdot}$ The metal dissolves, although very slowly, in aqueous acids with formation of this ion. Cadmion is colourless, and acts as a rather virulen poison on the lower and higher organisms. Its heat of formatio from the metal is 77 *kj*.

The cadmium salts in aqueous solution are distinguished by th fact that many of them are considerably less dissociated into ions than the corresponding salts of the other divalent cations. This is especiall noticeable in the case of the halogen compounds.

From the aqueous solutions of the cadmium salts alkali hydroxide precipitate white cadmium hydroxide, which is insoluble in an exces of the precipitant. This is in agreement with the general increase of the basic properties with increasing combining weight in the case of similar elements. Cadmium hydroxide is soluble in excess of ammonia. The solution contains complex cadmium-ammonia ions, $Cd(NH_3)_n^{\cdot\cdot}$.

By heating the hydroxide, and by the combustion of the metal in the air, cadmium oxide is obtained as a brown powder, which readily dissolves in acids to form cadmium salts.

Of the salts the sulphate should be mentioned. This still exhibits some similarity to the sulphates of the magnesium series, but also considerable divergence. Thus, it crystallises at the ordinary temperature in accordance with the formula $3(CdSO_4) . 8H_2O$, for which there is no analogy known in the case of the true "vitriols." The formation also of the typical double salt with potassium or ammonium sulphate does not take place quite readily.

The sulphate is readily soluble in water; in the case of the salt with $\frac{8}{3}$rds molecules of water of crystallisation the temperature has very little influence on the solubility. It is used in medicine, and is also employed for the construction of electrical "standard cells."

The *halogen compounds* of cadmium exhibit especially clearly the above-mentioned slight dissociation in aqueous solution. Of the three compounds, cadmium chloride is most, cadmium iodide least, dissociated. The latter salt forms crystalline laminæ of a pearly lustre, which are soluble in alcohol. On account of this property it is employed in photography as an iodising salt.

* Apart from the small conductivity, the following experiment demonstrates very clearly the slight degree of dissociation of cadmium iodide. If cadmium hydroxide is brought together with water and litmus or phenolphthalein, no alkaline reaction can be detected, because

the hydroxide is too slightly soluble. The same thing is observed on using a solution of potassium nitrate or sulphate instead of water. If we take a neutral solution of potassium *iodide*, however, a strong alkaline reaction is obtained on shaking up. The reason of this is that the cadmion which passes into solution from the hydroxide is converted into undissociated cadmium iodide. A fresh quantity of hydroxide must therefore pass into solution, and this must go on till equilibrium is attained. In this process the hydroxidion of the hydroxide remains over (along with potassium from the potassium iodide), and the solution must exhibit the reaction of hydroxidion, *i.e.* must react alkaline. In formulæ we have $Cd(OH)_2 + 2I' = CdI_2 + 2OH'$.

Cadmium Sulphide, CdS, is obtained as a fine yellow precipitate on passing sulphuretted hydrogen into a neutral solution of a cadmium salt. If the solution is acidified, precipitation occurs nevertheless, and a very considerable amount of acid must be added before sulphuretted hydrogen ceases to produce a precipitate. Similar chemical equilibria are obtained to those described in the case of zinc sulphide (p. 623), with this difference, however, that the concentration of hydrion necessary for equilibrium must be very much greater than in the case of zinc.

* If we have a solution in which cadmium sulphide has just been formed, and we add potassium iodide (or any salt containing iodidion), the cadmium sulphide immediately passes into solution. The reason of this is again that owing to the formation of undissociated cadmium iodide, cadmion disappears from the solution, and must be replaced by the dissolution of a fresh portion of the precipitate.

On account of its pure yellow colour, cadmium sulphide is used in painting under the simple name "cadmium," since other cadmium compounds are not employed as pigments.

* An amalgam of cadmium and mercury is employed by dentists as a filling for teeth, because it possesses the property of being soft and easily moulded for a short time after being prepared, but of very soon solidifying to a coherent, hard mass. This depends on the fact that the compound of the two metals is a crystalline substance, which is hard at the ordinary temperature, but which can be easily supercooled. In the soft mass, therefore, we have a superfused amalgam. When crystallisation has commenced it proceeds slowly through the whole mass, which thereby becomes hard.

CHAPTER XXXII

COPPER

General.—Between the metals of the new group, which is called after copper, and those of the former groups, many points of relationship exist. The circumstance that most of the heavy metals can form several series of compounds, *i.e.* ions of different valency, causes a crossing and interweaving of these mutual relationships which render it impossible to draw up a simple list of the elements in such a way that the most nearly related always stand together. For indeed, on following out one of the existing series, other ones must be interrupted; for the sum of these mutual relationships cannot be represented by means of a straight line, but only as a much-branched river system, or still better perhaps, as an arterial system exhibiting manifold anastomosis.

Thus in copper we have, on the one hand, a metal which in certain compounds shows itself to be related to the elements of the magnesium and iron series, while other compounds exhibit close relationships to silver and mercury. We have already frequently met with such ambiguity of behaviour, *e.g.* in the case of iron, and especially of manganese; it points to the fact that a systematisation of the chemical elements according to a single scheme is impossible, for a really exhaustive system must necessarily contain all the existing relationships, and must, therefore, be of such a form that these diversities receive adequate expression. The satisfactory solution of this problem has not as yet been attained, and we must at the present time get over the difficulty by pointing out, when necessary, the various relationships existing.

Copper.—Of the heavy metals already discussed, copper is the first that is found in any considerable quantity in the metallic state on the earth, and it belongs, therefore, together with silver and gold, to the metallic elements which have been longest known. It is distinguished from all other metals by its bright red colour, which, however, is seen only on fresh surfaces. Even in a very short time these become covered with a dark coating of oxygen or sulphur compounds, which, although it does not destroy the metallic lustre, changes the rose-red colour of the pure metal into the brown-red, which is usually called copper-red.

Copper melts at 1050°, has the density 8·9, and is, at the ordinary temperature, a tenacious metal which can be mechanically moulded, and which resists well the influences of the atmosphere and of moisture. On being exposed for a lengthened period to moist air, it is true, it becomes covered with a layer of oxygen compounds; this, however, remains very thin, and effectually protects the metal underneath. At a red-heat copper combines fairly rapidly with oxygen to form a black, brittle oxide, which readily breaks off in scales and exposes the underlying metal to fresh attack.

On account of its chemical resistibility, its good mechanical properties, and its melting point, copper is largely employed for utensils of all kinds. Another very extended sphere of application of copper depends on its great conductivity for the electric current. In this respect it is superior to all other accessible metals (silver is alone superior to it), and very large quantities of it are therefore employed in electro-technics. For this purpose it must be very pure, since the onductivity is greatly lowered even by very small amounts of foreign netals.

Besides being used in the pure state, copper is also extensively mployed for alloys. Brass has already been mentioned; others will e given later.

The combining weight of copper is $Cu = 63·6$.

The Ions of Copper.—Copper forms two kinds of elementary ons, the monovalent monocuprion, $Cu^{\cdot}$, and the divalent dicuprion, $u^{\cdot\cdot}$. The latter is allied to the divalent ions previously described, he former belongs to a new type. Of the two, the divalent one is by r the most frequent and better known, and, for that reason, shall be rst described.

The formation of dicuprion from metallic copper does not take lace nearly so readily as that of the ions of the metals hitherto escribed. Without the co-operation of the atmospheric oxygen, lute acids have no appreciable action on metallic copper, and only tric acid or hot concentrated sulphuric acid have a solvent action, hereby not hydrogen but a reduction product of the particular acid evolved. On the other hand, hydrogen gas acts on solutions of pper salts, eliminating copper from them with the simultaneous for- tion of free acid.

* Under ordinary conditions, this reaction occurs so slowly that it nnot be detected. If, however, the action of the hydrogen is acceler- ed by the presence of a catalyser, *e.g.* metallic platinum, the action n be detected.

* The dissolution of metals in nitric acid is accompanied by the luction of a portion of the acid. The process can be referred to

the scheme given on p. 597, if we write nitric acid as a hydroxyl compound of pentavalent nitrogen. The series is:—

Nitric acid, $HNO_3+2H_2O = N(OH)_5$
Nitrogen peroxide, $NO_2+2H_2O = N(OH)_4$
Nitrous acid, $HNO_2+H_2O = N(OH)_3$
Nitric oxide, $NO+H_2O = N(OH)_2$
Hyponitrous acid, $\frac{1}{2}H_2N_2O_2 = N(OH)_1$

In the oxidising action of nitric acid, from one to four oxidation units can take part, depending on which of the lower members the acid is converted into, and the equation has to be written accordingly. If, for example, it is desired to express the oxidation of copper to dicuprion with formation of nitric oxide (which is the predominant reaction on treating copper with nitric acid), we have the following. Each mole of copper requires two units in order to pass into dicuprion; one mole of nitric acid, however, yields three units. Consequently, we must allow two moles of nitric acid to react with three of copper. The three moles of copper, however, require further six moles of nitric acid in order to pass into normal nitrate; altogether then, eight moles of nitric acid act on three of copper:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

* Similarly, it is found that sulphuric acid on passing into sulphurous acid, yields two oxidation units, and these are exactly sufficient to convert one mole of copper into dicuprion. One mole more of sulphuric acid serves for the formation of the salt, so that we finally have

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

In its solutions, dicuprion is greenish-blue in colour. If any other colour is shown by a cupric salt, we must conclude that the undissociated portion of the salt is also coloured. This is, as a matter of fact, often the case.

For the higher organisms, dicuprion is a rather powerful poison, while moulds, for example, can flourish in presence of copper salts.

The heat of formation of dicuprion from the metal amounts to − 66 *kj*; it is therefore negative, while that of the metallic cations hitherto considered was positive. The difficulty of the formation of the ion from the metal, and the ease of the reverse transformation which we meet with in the case of copper, are connected with this fact.

Copper Hydroxide.—From the solutions of cupric salts, strong bases precipitate *cupric hydroxide*, $Cu(OH)_2$, as a bright blue substance which on being kept for some time under the solution, more quickly on heating, becomes dark brown, at the same time losing water and passing into cupric oxide, CuO. It may be asked how it is possible for a substance to lose water while lying under water, of which it ha therefore as much at its disposal as it requires. The answer is that cupric hydroxide is not at all a stable compound at the ordinary and at higher temperatures, and the fact that it is produced before the form which is most stable under the conditions, viz. copper oxide and water, is a case of the law of the prior formation of the unstable forms.

Copper hydroxide is not soluble in alkalis except in very small amount, when the solvent is very concentrated. Ammonia also precipitates cupric salts with formation of hydroxide; an excess, however, again effects dissolution. The liquid thereby becomes of a dark cornflower blue. This is a sign that a new ion has been produced; as a matter of fact, from the dark-blue solutions salts can be obtained in the solid state containing the cation $Cu(NH_3)_4^{\cdot\cdot}$.

Copper hydroxide is not a strong base; it is one of the weakest of the hydroxides of the divalent ions. This is shown in the distinct hydrolysis of its salts, in consequence of which the solutions of the salts of strong acids all react acid. Cupric salts of weak acids exhibit phenomena of decomposition; some, *e.g.* the carbonate, cannot be obtained at all in the normal condition, but only salts containing hydroxyl, or basic salts, are known.

Besides being formed by the decomposition of cupric salts, copper xide is also obtained by the direct oxidation of copper in the air at a ow red-heat. Cuprous oxide, the anhydride of cuprous hydroxide *vide infra*), is first formed, but this also passes into cupric oxide under he above conditions.

Copper oxide is very readily reduced to the metal by means of ydrogen with production of water. It has already been mentioned hat this reaction was used in order to determine the ratio of combination between hydrogen and oxygen. This same property of ready educibility conditions the use of copper oxide in organic elementary nalysis. The substance to be investigated is mixed with excess of opper oxide, the mixture placed in a tube and the whole heated, after bsorption apparatus for water (calcium chloride) and for carbon ioxide (caustic potash or soda lime) have been attached. By means f the oxygen of the copper oxide the carbon of the organic compound burned to carbon dioxide, the hydrogen to water. These products re collected and weighed, and from this the amount of the above lements contained in the organic compound (also weighed) can be etermined.

Any nitrogen which is present is evolved in the free state, and the mount can also be determined by collecting and measuring the gas.

Cupric Chloride.—Anhydrous cupric chloride, $CuCl_2$, is formed y the combustion of copper in a current of chlorine, as a yellowrown powder which dissolves in anhydrous solvents with a dark ellow colour, whereas its aqueous solution is blue or green, according the concentration. From the solution the salt with $2H_2O$ crystalses out; on account of adhering mother liquor, this generally appears green, but in the pure state it is bright blue. The hydrated salt on being heated loses hydrogen chloride along with the water, like many of the other chlorides of this group, and is converted into an oxychloride. The anhydrous salt experiences the same transformation on being heated in oxygen; chlorine is evolved at the same time: $4CuCl_2 + O_2 = 2Cu_2OCl_2 + 2Cl_2$. By means of hydrogen chloride, the oxychloride is again converted into the chloride: $Cu_2OCl_2 + 2HCl = 2CuCl_2 + H_2O$. This reaction is made use of for the manufacture of chlorine; the catalytic acceleration of the oxidation of hydrogen chloride with free oxygen (p. 166), also, is attributed to the alternate occurrence of these two processes in the mixture of oxygen and hydrogen chloride, but this view still lacks experimental foundation.

Concentrated aqueous solutions of copper chloride appear green. If fuming hydrochloric acid is added, a yellow-brown liquid is obtained. The latter colour is the individual colour of the undissociated copper chloride, the dissociation of which is reduced almost to zero by the large excess of chloridion. So long as considerable amounts of undissociated salt are present in the fairly concentrated solutions, the mixed colour formed by the yellow of the chloride and the blue of the dicuprion is produced. Very dilute solutions in which the dicuprion predominates, exhibit the blue colour of that ion. On being heated, dissociation is diminished; the yellow colour of the undissociated salt appears also to become more intense (p. 622), so that for this reason also, the solutions change colour towards the green. If we write with a solution of copper chloride on paper, the characters become yellow on being heated at those parts where the strongly coloured, anhydrous salt is formed, and on cooling disappear again where the pale-blue coloured hydrated salt is formed through the attraction of moisture from the air. This solution can therefore also be used as a "sympathetic ink" (p. 611), but must not be applied with a steel pen, because iron acts on solutions of copper with precipitation of this metal.

As has just been mentioned, cupric chloride readily forms oxychlorides with loss of chlorine. These compounds vary in composition according to the conditions of formation. The one best characterised is the compound $Cu_2Cl(OH)_3$, which occurs in nature as *atacamite*, and is also readily formed where chlorine compounds, water and oxygen, act on copper. It is a bright green substance which forms rhombic crystals, and is scarcely soluble in water. It dissolves readily in acids and in ammonia, as indeed could be expected from its composition.

Copper Sulphate.—Cupric sulphate or copper vitriol, $CuSO_4$, is obtained on the large scale by the oxidation of naturally occurring sulphur compounds of copper. It is a salt which crystallises in blue triclinic crystals with $5H_2O$, and which is similar to the other "vitriols" in its properties. According to the temperature, the salt takes up other quantities of water and exhibits forms which occur in the case of the sulphates of other divalent metals (cf. p. 569). It also crystallises along with potassium and ammonium sulphate in double salts with $6H_2O$. The water of crystallisation passes off fairly readily, a salt with $1H_2O$ at first remaining behind, which is more difficult to dehydrate. The anhydrous sulphate is dirty white in colour; in the air it absorbs water and again becomes blue. The dehydrated copper sulphate is sometimes used as a desiccating agent, especially for liquids, on account of the convenience of being able to tell when the desiccation is complete from the non-appearance of the blue colour in freshly added sulphate.

If an electric current is passed through a solution of copper sulphate, metallic copper is deposited as a coherent coating on the cathode. As it is particularly easy to obtain a good precipitate with copper (p. 615), the process is made use of not only for coating other objects with copper, but also for shaping objects in copper and thus of producing a sort of cold metallic casting. The deposit fills out very exactly the form of the cathode, and when it has acquired a certain thickness it can be removed as a coherent mass. For this reason it is used for taking casts of printing blocks. These are first cut in wood and then cast in warm gutta-percha or in very readily fusible metal cf. bismuth), and the cast is then made the cathode of an electric current in a solution of copper sulphate. The anode consists of copper n order that the amount of copper contained in the solution shall emain unchanged (p. 615). Non-conducting casts, such as those of gutta-percha or gypsum, are first covered with a conducting layer, *e.g.* y rubbing with graphite.

The same process is made use of for the purpose of purifying impure copper. The impure copper is then made the anode, and a thin heet of pure copper is used for the cathode. On this, very pure copper is deposited if a current of very small potential is employed, or the impurities either are not dissolved but sink to the bottom as anode mud," or they are not separated out at the cathode (*e.g.* iron), nd must be removed from the solution when they have accumulated o much. The copper, for example, which is used for electrical purposes, and which must be very pure, is treated in this way.

One can spare oneself the special generation of an electric current y making the separation of copper a part of the reactions in a voltaic ll. As a matter of fact, the process of electrical copper casting, *ectrotyping*, was discovered through copper sulphate being used as an xidising agent in a voltaic cell, whereby the deposited copper took e exact shape of the cathode.

Such a cell is represented in Fig. 114. *K* is the cathode of copper, a porous cell of fired clay which allows the current to pass, but ecks the mixing of the liquids, and *Z* is an anode of metallic zinc. is surrounded by a solution of copper sulphate, *Z* by a solution of nc sulphate. When, then, *K* and *Z* are connected by a metallic conductor L, the deposition of copper on K occurs, while an equivalent amount of zinc is at the same time dissolved from Z. During this process an electric current passes through the conductor in the direction of the arrow, and can be easily detected and measured by inserting a current indicator in the circuit.

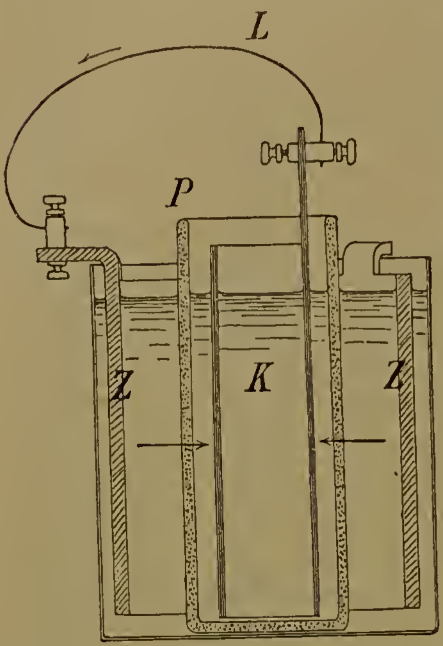


Fig. 114.

The chemical process, therefore, consists in metallic copper being deposited from the copper sulphate and zinc dissolving to zinc sulphate. If we write the equation of the ions, we have first of all: $Cu^{\cdot\cdot} + SO_4'' + Zn = Cu + Zn^{\cdot\cdot} + SO_4''$; omitting on either side the ion SO_4'', which remains unchanged, we obtain $Cu^{\cdot\cdot} + Zn = Cu + Zn^{\cdot\cdot}$. The process, therefore, simply consists in the copper and zinc exchanging their rôle as ions, or, since the ionic state is determined by the positive electrical charge, in the cuprion yielding up its charge to the zinc, which thereby passes into zincion, while the copper is deposited in the metallic state.

This process immediately occurs when metallic zinc is introduced into a solution of copper sulphate; copper is deposited and zinc is dissolved. An electrical current cannot, however, be obtained in this way. The reason of this is that the transference of the charges takes place everywhere within the liquid, so that it is not possible to lay hold of and conduct the electrical movement. In the arrangement shown in Fig. 114, which is called after its discoverer, the Daniell cell, the solution of the zinc and the deposition of the copper take place at separate points, and this becomes possible only when the necessary equalisation of electricity occurs through the medium of the liquid on the one hand, and of the conductor on the other.

Voltaic Cells.—In order that the above process, whereby ar electric current is generated in the Daniell cell, may occur, it is evident that the reactions on which the cell is based should occur even with out this special arrangement, since there would otherwise be no caus to make the process take place. Now, however, only those processe occur in which free energy is available; a voltaic cell is therefore a apparatus by means of which free chemical energy is converted int free electrical energy.

It will therefore be possible to construct other cells after th pattern of the Daniell, by replacing the zinc and the copper by othe metals placed in solutions of their salts and connected with on another. This is, as a matter of fact, the case; with every such combination a cell is obtained in which one of the metals is reduced from its salt and deposited in the metallic state, while the other is oxidised, *i.e.* is dissolved as ion. Which of the two connected metals will assume one or the other rôle, is found by introducing each metal into the solution of the other; one of the metals will then precipitate the other from its solution, while the other metal will leave the solution of the first unchanged. The precipitating metal is then always the anode, which also dissolves in the cell the same as in the direct experiment, and the precipitated metal is the cathode, for it is deposited in the cell in the same way as in the direct action. From these experiments it is found that a given metal can both precipitate and be precipitated; cadmium eliminates copper from solutions of copper salts, but is deposited from its solutions in the metallic state by zinc.

The law which obtains here can be expressed as follows: *It is possible to arrange all the metals in a single series in such a way that each precipitates all the metals following from their aqueous solutions, but is precipitated by each of the preceding ones.* On account of the electrical relations of this series, to be presently mentioned, it is called the *potential series* of the metals.

Electrical Potential.—The work which an electric current can perform, depends not only on the strength of the current or the amount of electricity which in unit of time passes through a section of the conductor, but on another magnitude as well, which is called the *potential*, the unit of which, fixed once for all, is called the *volt.* Thus an electric incandescent lamp, which is supplied by a current of one ampere (p. 193) at a potential of 50 volts, gives the same light as a lamp which uses a current of 5 amperes at 10 volts, while at a potential of 200 volts a current of 0·25 ampere is sufficient to produce the same effect.

From this example it is at once seen that the electrical work of a current is measured by the *product of strength of current and potential.* This has a great similarity to the performance of work by a falling mass of water; in this case also the work depends on the quantity of the water, and on the height of fall, and the amount of work which can be obtained with the same quantity of water is all the greater, the greater the height through which the water falls. To the *quantity of water* there corresponds the magnitude, which has been called *quantity of electricity*, and which can be measured, in accordance with Faraday's law (p. 192), by the amount of substance separated electrolytically on inserting an electrolytic cell in the circuit. To the *height of fall* there corresponds the property of electrical energy, which has just been called *potential.* The product of volt and ampere, which represents the work done in a second (because an ampere is a unit of electricity per second), is called a watt. A watt is equal to the work of 10^7 erg

(p. 23) in the second, and is therefore approximately equal to the work which is performed by a waterfall in which 100 gm. of water fall through a height of 1 metre in a second; it is therefore a rather small magnitude. For technical purposes, therefore, a unit a thousand times as large is generally employed, viz. the kilowatt, which is equal to 10^{10} erg in the second.

The Potential of Cells.—If we imagine various voltaic cells constructed after the pattern of the Daniell, in which zinc is always used as one metal along with various other metals, *e.g.* cadmium, copper, and silver immersed in solutions of their salts, each of these cells will be able to yield a current and perform work. In the process, zinc will dissolve and the other metal will be precipitated. If we allow each of the cells to do work until a definite amount of zinc, *e.g.* one mole, has been dissolved, the amounts of work will be different in the different cells, for the chemical energy which becomes available in the case of each is different. It will be greatest in the case of the silver-zinc cell and least in the cadmium-zinc cell, for of the three metals, silver is the easiest, cadmium the most difficult to reduce; of the work, therefore, which the zinc can perform in passing into zincion, most will remain over for the current in the case of the silver cell and least in the cadmium one.

The quantities of electricity, however, which are set in motion for the current by the dissolution of equal amounts of zinc in the different cells, is in all cases equal, since, according to Faraday's law, equal amounts of electricity must be transported with equal amounts of zinc, independently of what work the current otherwise performs. Since the amounts of work in the cells are necessarily different, the above differences must find their expression in the other factor of electrical work, *i.e.* the *potentials* of the cells must be different. This is shown by measurement to be the case; if such cells are constructed and their potentials measured with a volt-meter (an instrument which allows of the potential being directly read off by means of a pointer), the following values are obtained:—

Silver-zinc	1·57 volt
Copper-zinc	1·10 ,,
Cadmium-zinc	0·35 ,,

The above considerations can be extended. According to Faraday's law, the amounts of electricity which are set in motion are equal not only for equal amounts of zinc but also for equivalent amounts of all ions whatever (p. 194). The potential of the cells is therefore in all cases the measure of their power of doing chemical and electrical work, or the measure of the free energy of the chemical reaction occurring in the cell. Indeed, the measurement of the electrical potential is at the present time the most fruitful method of determining this important and not easily accessible magnitude.

On constructing a cell containing the above three metals and also the other possible cells, the following values of the potentials are obtained:—

Silver-copper	0·47	volt
Silver-cadmium	1·22	,,
Copper-cadmium	0·75	,,

On comparing these values with the former, it is found that the potential of the combination silver-zinc is equal to the sum of the potentials silver-copper plus copper-zinc or silver-cadimum plus cadmium-zinc, etc. Writing the values

Silver = 1·57 volt
Copper = 1·10 ,,
Cadmium = 0·35 ,,
Zinc = 0·00 ,,

we find that the potential of any combination of these metals is equal to the difference of the corresponding numbers. These numbers may therefore be called the potentials of the single metals, in which case, certainly, the zero, Zn = 0, has been arbitrarily chosen. This, however, has no influence on the result, for if any other metal is put equal to zero, and the corresponding values of the potential are calculated with due regard to the sign, another series is obtained which exhibits the same differences between the separate members, and has the same meaning, therefore, as the former series.

This series is the numerical expression of the potential series (p. 633); it is the expression of a fundamental property of the metals.

The numbers depend on the temperatures, but their relative positions do not greatly change within the range of temperatures investigated; as regards this point, however, our knowledge is as yet rather scanty.

The following table gives a more complete list of potentials. In this case zinc has not been taken as the zero, but another zero has been chosen which gives expression to the actual change of the free energy in the passage from the metallic to the ionic state. We cannot explain here how this zero has been derived, and this is of no importance, in the first instance, since we are concerned only with the differences, and these are independent of the zero.

Cæsium	—		Tin	—	
Rubidium	—		Lead	− 0·10	volt
Potassium	—		Hydrogen	− 0·25	,,
Sodium	—		Antimony	—	
Magnesium	+ 1·24	volt	Bismuth	—	
Aluminium	1·03	,,	Arsenic	—	
Manganese	0·82	,,	Copper	− 0·59	,,
Zinc	0·51	,,	Mercury	− 1·03	,,
Cadmium	0·16	,,	Silver	− 1·06	,,
Thallium	0·11	,,	Palladium	− 1·07	,,
Iron	0·09	,,	Platinum	—	
Cobalt	− 0·02	,,	Gold	—	
Nickel	− 0.02	,,			

Where no number is given, only the position of the metal in the series is known, but not the numerical value of the potential.

Copper Nitrate crystallises in blue crystals containing $3H_2O$, and cannot be freed from its water of crystallisation without at the same time losing acid. The basic copper nitrate, $Cu_2(NO_3)(OH)_3$, is obtained by the action of copper carbonate on the normal nitrate, or by the partial precipitation of the latter with a carbonate (the carbonic acid of which escapes); it is a blue-green powder, very difficultly soluble in water, the composition of which corresponds to that of atacamite, and which is remarkable as being one of the few nitrates which are difficultly soluble in water.

* If some crystals of the hydrated, normal copper nitrate are wrapped in tinfoil, the latter is oxidised, and a vigorous reaction takes place with scintillations. The same reaction has sometimes given rise to dangerous fires in powder manufactories, where copper nitrate can be formed by the action of saltpetre on the metal of the vessels.

Copper Carbonate.—On precipitating solutions of a copper salt with carbonates, blue to green precipitates of basic copper carbonate are obtained; the corresponding reactions were explained in the case of magnesium (p. 535). In nature, also, normal copper carbonate does not occur, but only the basic salt. *Malachite*, a green mineral which is used for objects of art, has the composition $Cu_2(CO_3)(OH)_2$; *azurite*, a dark-blue basic carbonate, which has a similar application, is $Cu_3(CO_3)_2(OH)_2$. Both are valuable copper ores.

Copper Acetate, $Cu(C_2H_3O_2)_2 + H_2O$. This salt has long been known by the name verdigris.[1] It is obtained by alternately covering copper plates with residues from the preparation of wine and exposing to oxidation by the atmospheric oxygen. By means of the latter, acetic acid is formed from the alcohol of the residues, and the copper is converted into the acetate. This is deposited as the basic salt on the copper plates in bluish-green masses, and is placed in this form on the market for use as a pigment. The normal salt is obtained by crystallisation from dilute acetic acid, and forms dark-green crystals, which are also employed for painting and dyeing.

Copper Sulphide, CuS, occurs in nature as indigo copper or covellite, and is formed by the precipitation of cupric compounds with sulphuretted hydrogen. It is thus obtained as a brown-black powder of not very constant composition, as it has a great tendency to pass into cuprous sulphide, Cu_2S, and free sulphur. It is practically insoluble in dilute acids; copper can therefore be precipitated by sulphuretted hydrogen from acid solutions, a behaviour which is made use of for the analytical separation of copper (and the other metals of this group) from those of the iron group.

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[1] The coatings of basic carbonate which are formed on copper in the air are also sometimes called verdigris.

* On account of the above mentioned indefiniteness of the composition, the precipitated copper sulphide cannot be weighed directly. It is dissolved in nitric acid, and the nitrate produced is either precipitated with caustic potash, whereby brown copper oxide (p. 628) is obtained, or it is decomposed by the electric current, whereby metallic copper is deposited. The copper sulphide can also be ignited in a current of hydrogen, whereby cuprous sulphide, Cu_2S, which has a constant composition, is formed.

* For the electrolytic deposition, the apparatus shown in Fig. 115 may be used. The solution is placed in a platinum dish, which is made the cathode of an electric circuit (accumulator and resistance); a thick platinum wire, coiled round several times, is employed as the anode. The resistance is so regulated that a current of about 1 ampere is obtained; the copper then separates out in the course of a few hours as a rose-red precipitate on the platinum.

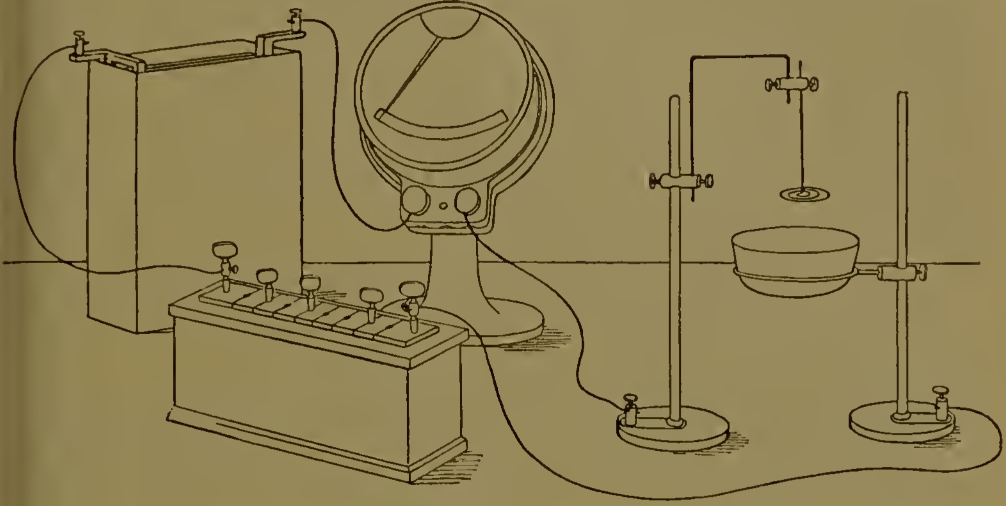

Fig. 115.

* **Copper Ferrocyanide—Osmotic Pressure.**—When dicuprion and ferrocyanidion come together in aqueous solution, a red-brown, amorphous precipitate of cupric ferrocyanide, $Cu_2Fe(CN)_6$, is produced, which, on account of its strong colour, can be detected even in very small amount, and is therefore used for the identification of copper.

While the analytical importance of this substance is rather small, it has, in another respect, attained to very great importance in the development of chemistry. This is due to the following property.

If a porous clay cell is first soaked with a solution of copper sulphate, and if this be then removed and a solution of potassium ferrocyanide placed in the cell, a precipitate of copper ferrocyanide is formed in the pores of the cell and closes this up in a special manner. If a cell of this kind, such as was first prepared by W. Pfeffer in 1877, is filled with pure water, it behaves essentially like any ordinary clay cell, for under slight pressure, the water flows through, only mor slowly than when the precipitate is absent. If, however, instead o the pure water an aqueous solution, *e.g.* of ordinary sugar, is place in the cell, this does not, in the first instance, filter through. If th pressure is increased, percolation commences at a definite pressure, bu it is not the sugar solution that filters through but pure water.

If the experiment is performed with different solutions of sugar it is found that a definite pressure is necessary in each case in orde that the water may pass through, and this pressure is proportional t the concentration of the solution.

If, after being closed and a manometer attached, the cell is place in pure water, the latter continues to pass through the cell-wall unti the same pressure is produced as that under which the water coul be forced through the cell-wall.

Various other substances behave in a manner similar to sugar they are kept back by the cell-wall and generate a pressure. There ar substances, however, which are not kept back by the cell-wall; these also, do not generate a pressure (or only a comparatively small one when they are partially retained).

We must conclude, therefore, that the pressure is due to the dissolved substance; the water cannot give rise to it because it can pass through the cell-wall.

On comparing solutions of different substances which do not pass through the cell-wall, with respect to the pressure which they produce, it is found that *the same pressure is produced by those solutions the concentrations of which are in the ratio of the molar weights of the dissolved substances.* These pressures, therefore, which are are called *osmotic pressures*, could be used for the determination of the molar weight of dissolved substances, in the same manner as the depression of the freezing point and the lowering of the vapour pressure (p. 155). The experimental difficulties in the carrying out of such measurements, however, are very great.

The temperature exercises an influence on the osmotic pressure; under ordinary conditions, the latter increases about $\frac{1}{3}$rd per cent for every degree.

On the whole, therefore, the osmotic pressure follows similar laws to the gas pressure; the latter is also proportional to the concentration or density of the gas (Boyle's law, p. 67), and for every degree increases by 1/273, *i.e.* about $\frac{1}{3}$rd per cent (Gay-Lussac's law, p. 68).

The resemblance, however, extends still further. If, for example, the osmotic pressure is determined which is exerted by a definite solution of carbon dioxide, it is found to be just as great as that exerted by the same amount of carbon dioxide when it occupies in the gaseous state the same volume as the solution. Thus far, therefore, a dissolved substance behaves as a gas, and its osmotic pressure is represented by the same formula, $pv = RT$, as the pressure of a gas; more especially, also, the constant R has the same value. Now, it was stated on p. 89, that at 0° a mole of every gas exerts a pressure of one atmosphere when it occupies a volume of 22,400 cc. or 22·4 lit. If a mole of any substance is dissolved to a volume of 22·4 lit., its solution exhibits at 0° the osmotic pressure of one atmosphere.

These laws are valid not only for aqueous solutions but for all solvents. They have not, it is true, been proved by direct experiment for the other solvents, but they have been indirectly.

On comparing the laws of osmotic pressure which have just been enunciated with those of the changes of the freezing point and vapour pressure (p. 155), a large measure of agreement is found. This is not accidental, but can be established on theoretical grounds, so that if the laws of, *e.g.*, the depression of the freezing point are given, those of the others, *e.g.*, of the osmotic pressure, can be deduced from them. The connection depends on the fact that each of these phenomena can be used for the performance of a definite amount of work, and that in virtue of the theorem of the impossibility of a *perpetuum mobile* of the second kind (p. 133), the work yielded by a given change of state must be the same in all cases, no matter in what way it is obtained. If now the amount of work be calculated for the different cases (freezing, vaporisation, filtration through a cell-wall) and the results compared, the formulæ are obtained by means of which the corresponding change of the vapour pressure or of the freezing point can be calculated from any measured value of the osmotic pressure, and *vice versa*. Thus it is found that under comparable conditions the above three magnitudes remain proportional to one another.[1]

Finally, we must answer the question whether the laws of osmotic pressure hold only for such cell-walls as are formed of copper ferrocyanide. The answer is that the laws have a general validity for all septa which do not allow the dissolved substance to pass through. This property of selective permeability is possessed, more especially, by the walls of plant and animal cells, and with these the laws of osmotic pressure have in many cases been tested, and partly, indeed, discovered.

Cuprous Compounds.—Compounds in which the copper appears as monovalent are numerous, although the corresponding monovalent cuprion, $Cu^{\cdot}$, is scarcely known. In other words, compounds belonging to such a monovalent series are known in the solid state, but not, in a tate of purity, in solution.

In the oxidation of heated copper in the air, a red oxide is first ormed, the composition of which is Cu_2O, and which is therefore called uprous oxide. On being further heated in the air, it is converted into black cupric oxide; on removing this black coating, however, from a piece of oxidised copper, it is found to be generally red coloured o the side next the metal, *i.e.* to consist of cuprous oxide.

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[1] Full information will be found in the author's *Outlines of General Chemistry*, ranslated by J. Walker (Macmillan), and also in *Introduction to Physical Chemistry* by ames Walker (Macmillan).

The corresponding cuprous hydroxide, $Cu_2(OH)_2$, or Cu(OH), i obtained as a brick-red powder by the decomposition of cuprou chloride, to be presently mentioned, with caustic potash or soda.

In nature cuprous oxide occurs as red copper ore, and is a ver highly valued ore on account of its richness in copper; it can readil be converted into metallic copper by reduction with charcoal.

Cuprous oxide is also formed as the product of reduction Fehling's solution with grape-sugar and similar substances (p. 643), an can be prepared in this way. In moist air it is oxidised to cupric oxid or to basic carbonate.

On treating cuprous oxide or hydroxide with acids, not the corre sponding cuprous, but the cupric salts, are generally formed, and hal of the copper is deposited in the metallic state as a blackish-red powde With sulphuric acid, for example, the reaction takes place according t the equation $Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O$. On considerin the ions the process can be interpreted as taking place in such a wa that cuprous sulphate is first formed, the monocuprion of whic however, immediately undergoes transformation into dicuprion an metallic copper: $2Cu^{\cdot} = Cu^{\cdot\cdot} + Cu$. The solution contains dicuprio to a preponderating extent, but it is in accordance with the genera relations to assume that it is a case of chemical equilibrium betwee the two ions and the metallic copper, in which a large concentratio of dicuprion is opposed by a very slight concentration of monocuprion As a matter of fact, it has been shown that on bringing metallic coppe into contact with a solution of copper sulphate, some of the forme passes into solution with formation of cuprous sulphate, *i.e.* o monocuprion.

If instead of sulphuric acid a halogen hydracid, thiocyanic acid, o some other acid which can form a very difficultly soluble cuprous salt is taken, the above decomposition does not take place, and the respectiv cuprous compounds are formed. This is explained by the fact tha monocuprion is present only in a negligibly small amount in the solu tion produced, since, of course, the salts are difficultly soluble. Th decomposition of monocuprion into dicuprion and metal can therefor take place only to an inappreciably slight extent.

Cuprous Chloride is a white salt, only very slightly soluble i water; it can be obtained by boiling a solution of cupric chloride i strong hydrochloric acid with copper powder. The colour at firs darkens, but a yellowish liquid is finally obtained, which on bein poured into much water deposits a snow-white precipitate of cuprou chloride. This must be washed as far as possible with exclusion of air as it otherwise rapidly passes into cupric chloride (p. 630).

This reaction is the reverse of the one given before; whereas in th previous case monocuprion decomposes into dicuprion and metalli copper, we have in this case the reverse transformation of cupric salt with metallic copper into cuprous salt. The reason is that in the hydrochloric acid solution monocuprion is present only in very slight amount; indeed, the fact that cuprous chloride, which is almost insoluble in water, dissolves in hydrochloric acid, proves that in this case the chloride is either dissolved as such (without dissociation), or that a compound of the two constituents, a hydrochlorocupric acid, has been formed. No investigation has as yet been carried out as to how far the one or the other possibility predominates.

In ammonia also cuprous chloride dissolves to a colourless liquid, in which cuproammonion, $Cu(NH_3)^{\cdot}$, is contained. The chloride of this ion, $CuNH_3Cl$, can be obtained in colourless, regular crystals by boiling a solution of ammonium chloride with copper powder and allowing the liquid produced to cool slowly. The aqueous solution becomes almost immediately blue in the air, oxygen being absorbed.

Both solutions of cuprous chloride, the acid as well as the ammoniacal, absorb a considerable amount of carbon monoxide. This appears to be rather firmly bound, but can be removed from the liquid by continued pumping. We are dealing in this case with the formation of a complex cation, similar to the complex ion produced from diferrion and nitric oxide (p. 582), which, like this, is not very stable, and possesses an appreciable dissociation pressure. The reaction is used for the determination of carbon monoxide in gaseous mixtures, but must, for the reasons just mentioned, be employed with some care.

Cuprous Bromide, $CuBr$, is very similar to cuprous chloride.

Cuprous Iodide is formed along with free iodine, when dicuprion nd iodidion come together in solution, according to the equation $2Cu^{\cdot\cdot} + 4I' = 2CuI + I_2$. In this process we can regard the dicuprion s losing a positive charge, and thereby neutralising the negative charge f one iodidion. The monocuprion produced at once forms solid uprous iodide, with a second quantity of iodidion, and separates out. f a reducing agent is added at the commencement, whereby the icuprion can be converted to monocuprion, cuprous iodide alone without free iodine is deposited. This is effected, for example, by sulphurous cid or an acid solution of ferrous sulphate.

Since the cuprous iodide is soluble only to an exceedingly slight xtent, even very small quantities of iodine can in this way be separed from a solution, and the method is employed commercially for taining iodine from the mother liquors containing iodidion along ith comparatively large quantities of other halogens.

Cuprous iodide is a reddish-white, heavy powder which yields pric oxide and iodine by distillation with pyrolusite, and potassium dide and cuprous oxide by boiling with caustic potash. It dissolves ammonia similarly to cuprous chloride.

* The interaction between iodidion and dicuprion, described above, es not occur instantaneously, but with a measurable velocity which

becomes very small with increasing dilution. Thus very dilute solutions of copper sulphate and potassium iodide can be mixed without iodine at once separating out. After some time, however, the cuprous iodide begins to separate out, and free iodine makes its appearance. Chemical equilibrium is then established between the substances present, and the reaction can become complete only by the withdrawal of the one or the other constituent from the solution.

Copper Thiocyanate, CuSCN, is allied to the substances just described with respect to its difficult solubility, and therefore also the conditions of its formation. If thiocyananion and a reducing agent, such as sulphurous acid, are introduced into a solution containing dicuprion, white cuprous thiocyanate is deposited. The reaction corresponds exactly to that described in the case of cuprous iodide, so that it need not be again explained. It is made use of for the separation of copper from other metals; the precipitated and dried cuprous thiocyanate is mixed with sulphur and ignited in a current of hydrogen, whereby it is converted into cuprous sulphide.

Other Cuprous Compounds.—*Cuprous sulphide* occurs fairly abundantly in nature as *copper glance*, and is an important copper ore. It is a dark coloured substance which forms rhombic crystals, fuses fairly readily, and does not conduct electricity. Its formation from cupric sulphide by heating in hydrogen has already been mentioned. On being roasted in the air it is converted into a mixture of cupric oxide and copper sulphate.

Dicuprion behaves towards cyanidion in the same way as towards iodidion. If the two ions come together in solution free cyanogen is evolved, and cuprous cyanide is deposited as a white precipitate: $2Cu^{\cdot\cdot} + 4CN' = 2CuCN + (CN)_2$. This is a convenient method of obtaining cyanogen gas. In order to have a copious evolution of gas it is only necessary to heat together equivalent solutions of copper sulphate and potassium cyanide.

Complex Copper Compounds.—We have already spoken of the formation of a complex compound of dicuprion and ammonia, which is characterised by the production of a dark blue coloration in the mixed solution. In this the new ion $Cu(NH_3)_4^{\cdot\cdot}$ is formed, the salts of which are obtained by adding excess of ammonia to the solutions of the respective copper salts.

Of these salts the best known is the sulphate, $Cu(NH_3)_4SO_4$, which is easily obtained by adding ammonia to a concentrated solution of copper sulphate until the solution has again become quite clear, and then pouring a layer of alcohol on the top. The salt is only very slightly soluble in alcohol, and is deposited in well-formed, dark-blue crystals as the alcohol slowly diffuses into the underlying liquid. In the same way various other salts of the same ion can be obtained. Solutions of these salts are used in combating certain parasites (mildew) on vines.

Copper forms other complex compounds of a similar colour on adding excess of alkali to cupric salts in presence of certain organic compounds, *e.g.* sugar or tartaric acid. In this case also a dark-blue liquid is produced from which a salt of the same colour can be obtained. In these salts acids containing copper are present, the composition of which depends on that of the substance employed, and cannot be discussed here. In general the property of forming such compounds is found in the same organic hydroxyl compounds as hinder the precipitation of ferric oxide by bases (p. 582).

Of such compounds the best known is *Fehling's solution*, which is obtained by adding tartaric acid and excess of caustic potash to a solution of copper sulphate. It is a dark-blue liquid, which is changed by various reducing agents in such a manner that it deposits a precipitate of red cuprous oxide (p. 640). It can serve, therefore, for the detection of such substances, and it is used for this purpose in analysis, *e.g.* for the detection of grape-sugar in urine.

In the cuprous series some complex copper compounds have been already mentioned. It has still to be remarked that cuprous cyanide dissolves in potassium cyanide to form a colourless liquid, from which he complex salt $KCu(CN)_2$, the potassium salt of cuprocyanidion, is obtained. This solution is very stable, and contains exceedingly little uprion, so that all solid copper compounds, even copper sulphide, dissolve in potassium cyanide with formation of this complex salt. Advantage is also taken of this behaviour in analysis.

Copper also forms a number of complex compounds in which ulphur plays a part, and which are derived from sulphurous and hiosulphuric acids. This reference to their existence must suffice here.

Metallurgy of Copper.—On account of the large consumption f copper in the arts, its manufacture from the naturally occurring ores s an important industry. So long as we are dealing with oxygen res, red copper ore, or the basic carbonates, reduction with charcoal, hich takes place very readily, is all that is necessary. In the case of ne sulphurous ores, the most important of which are copper pyrites nd variegated copper ore, the task is more complicated. Both these res are compounds of copper sulphide with iron sulphide, and the reparation of pure copper requires at the same time the elimination of ulphur and iron. This is rendered more difficult by the fact that the ulphur combines much more firmly with copper than with iron, so hat it can be removed only with difficulty. On being subjected to an xidising process of roasting, ferrosoferric oxide is chiefly formed along ith cuprous sulphide, and by fusing this mixture with the addition f siliceous substances, a slag consisting essentially of iron silicate and mixture or an alloy of copper and cuprous sulphide, is obtained by peating the operation. When the amount of sulphur has become ufficiently small, the crude copper (black copper) is cast into plates nd subjected to electrolysis in an acid solution of copper sulphate, with a piece of copper-foil as cathode. In this way pure copper is obtained, and the copper sulphide, which along with the other impurities forms the anode mud, is again fused along with other portions of the ore.

The development of the method of electrolytic deposition has further led to the extraction of the copper ores in the wet way, the metal being separated electrolytically from the solutions of copper salt obtained. For this purpose ferric salts are mostly used, which dissolve the cuprous sulphide with formation of cupric salt, themselves being reduced to ferrous salts, and sulphur being deposited.

On re-fusing the copper, cuprous oxide is formed, which dissolves in the liquid metal, but on cooling again separates out and renders it brittle. For this reason the copper directly before being cast must be subjected to a reducing treatment (stirring with a pole of wet wood). If the reduction is carried too far the tenacity of the copper is impaired, presumably through the conversion of traces of other metallic oxides into the metallic state. This last operation must, therefore, be performed with care and frequent sampling.

CHAPTER XXXIII

LEAD

General.—Lead is allied to strontium and barium in like manner as zinc and cadmium are allied to magnesium. Calcium, which exhibits relations of isomorphism in both directions, stands in the middle. On he other hand, lead is decidedly a heavy metal, and forms an insoluble, lark-coloured sulphur compound.

In nature lead is fairly widely distributed. Its most important naturally occurring ore is lead sulphide, from which by far the largest amount of the metal is obtained. The carbonate and the sulphate, which are isomorphous with the corresponding salts of strontium and barium, are also found.

Metallic lead has been known from olden times, as it can be readily obtained from its ores. Its many applications depend, on the one hand, on its low melting point, 326°, and its great density, 11·4, and, on the other hand, on its softness and consequent plasticity. The last property renders it possible, especially at a somewhat higher tempera-ure, to form lead by pressure like a plastic mass, and in this way to produce wire, tubing, and such like.

In moist air lead oxidises very rapidly, but only superficially, so hat on the whole it is fairly resistant. It should be mentioned here hat it resists the action of perfectly pure water much less than that f ordinary spring or river water. This is due to the fact that in the ormer case, under the joint action of water and atmospheric oxygen, ead hydroxide is produced, which is slightly soluble in water, and herefore does not protect the lead. In impure water, which contains ulphanion and carbanion, the corresponding lead salts are formed, which have an extremely small solubility, and form a firmly adhering ayer on the lead. Thus lead pipes can be quite well used for the rdinary water supply, but not for distilled water.

The combining weight of lead has been determined by the conver-on of the metal into the oxide, and *vice versa.* It has been found to e Pb = 206·9.

Plumbion.—Lead forms only one divalent elementary ion, but esides this several containing oxygen, and also complex ions.

Plumbion, $Pb^{\cdot\cdot}$, is colourless, and in its compounds resembles barion in many respects. It is a powerful poison for higher organisms, and through accumulation is very harmful when repeatedly taken into the system even in small doses. For this reason workmen who have to work with lead are constantly exposed to the poisonous action, and great attention and cleanliness are required in order to restrict the danger.

The heat of formation of plumbion from the metal is + 2 *kj*.

Corresponding to its position in the potential series, lead has no special tendency to pass into the ionic state. Free acids are not appreciably decomposed by lead, so that oxidising agents must be employed in order to dissolve it. The best solvent for metallic lead is nitric acid, which forms one of the few readily soluble lead salts, most of the lead salts being difficultly soluble.

From the solutions of the salts, bases give a white, flocculent precipitate of *lead hydroxide*, $Pb(OH)_2$, which does not dissolve in excess of ammonia, but is soluble in excess of alkali. The reason is the same as in the case of alumina, which behaves in a similar manner. By splitting off hydrion, lead hydroxide can form anions of the composition PbO_2'' and $HPbO_2'$, the alkali salts of which are soluble in water.

Lead hydroxide is slightly soluble in water. It is readily formed when lead, water, and atmospherie oxygen come together. Strange to say, in this oxidation, as in many others which occur with free oxygen in presence of water, hydrogen peroxide is formed at the same time. Measurements have shown that the amount of peroxide corresponds to that of the lead hydroxide, so that the reaction has to be written as follows :—

$$Pb + 2H_2O + O_2 = Pb(OH)_2 + H_2O_2.$$

* It is probable that the first product of the reaction is a single substance, perhaps a compound $Pb(OH)_4$, which decomposes into $Pb(OH)_2$, and H_2O_2. This reaction would then be another example of the fact that the unstable compounds are usually formed before the stable. This view, however, is rendered somewhat doubtful by the properties of the anhydride of the assumed compound $Pb(OH)_4$, viz. lead peroxide PbO_2, which is a well-known stable substance.

* The formation of hydrogen peroxide, or of other compounds belonging to the peroxide type, has been proved in the case of many oxidations by free oxygen, so that it appears to be the rule. The peroxide, certainly, generally decomposes so rapidly with evolution of free oxygen that its whole amount can never be determined, and only very slight traces are found if special precautions are not observed. The rational interpretation of these long neglected but very general phenomena is given by the law above-mentioned of the occur-

rence of the unstable forms; this view, however, still awaits general application.

Lead hydroxide loses water very readily and passes into the pale-yellow coloured lead oxide, PbO. The same compound is obtained in any desired amount by heating lead to above its melting point in the air; if the temperature is raised above its melting point, it forms reddish-yellow, lustrous scales, and in ordinary life is called litharge. It is used for many purposes in the arts, *e.g.* in the manufacture of glass, for the preparation of varnish, in dyeing, etc.

Lead Chloride, $PbCl_2$, is slightly soluble in cold water, more soluble in hot, and crystallises in anhydrous needles. It unites with lead oxide to form basic salts, which are obtained by heating ammonium chloride with litharge; they are of a pale yellow colour, and are used as a pigment under the name *Naples yellow.*

Lead bromide is similar to the chloride, only still less soluble.

Lead iodide, PbI_2, is still more difficultly soluble. It crystallises from hot saturated solutions in laminæ of a gold lustre; precipitated from a dissolved lead salt in the cold by means of an iodide, it is obtained as a yellow powder. It undergoes slight decomposition in light, so that a mixture of lead iodide and starch when exposed to sunlight rapidly becomes dark through formation of starch iodide. It unites with potassium iodide to form a double salt, which is stable only in contact with solutions which contain a large excess of potassium iodide; it is decomposed by pure water with separation of lead iodide.

Lead Nitrate, $Pb(NO_3)_2$, crystallises anhydrous in forms of the regular system, and is isomorphous with barium nitrate. It is easily obtained by dissolving lead or lead oxide in dilute nitric acid; by concentrated acid it is precipitated from its solutions, owing to the increase of the concentration of nitranion. Strong nitric acid is therefore almost without action on the metal, because the nitrate produced forms a protecting layer.

On being heated, lead nitrate decomposes into lead oxide, oxygen, and nitrogen peroxide: $2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$. This behaviour is made use of for the preparation of nitrogen peroxide (p. 328).

Lead Sulphate, $PbSO_4$, is a white salt extremely difficultly soluble in water, and is always formed when plumbion and sulphanion come together in solution. It is very similar to barium sulphate, but by reason of its greater density it is deposited more rapidly than it from solutions. It is readily soluble in a solution of ammonium tartrate containing excess of ammonia, and is thereby easily distinguished from barium sulphate. This solubility depends on the formation of a complex acid, the lead uniting with the anion of tartaric acid to form a complex compound. This, again, is another case of the formation of organic hydroxyl compounds containing metals, which has been several times mentioned (pp. 572 and 643). Since plumbion is withdrawn from the solution through the formation of this complex, lead sulphate must pass into solution in order to cover the loss, and this goes on either until all the lead sulphate is dissolved, or until chemical equilibrium has been established between the different components of the solution and the solid salt.

Lead sulphate occurs in nature in rhombic crystals which are isomorphous with those of heavy spar and celestine, and which are called *anglesite* or *lead vitriol.* The salt also occurs as an intermediate product in working up lead sulphide for metallic lead.

To the difficult solubility of lead sulphate is due the use of lead for lining the reaction chambers and concentrating pans used in the manufacture of sulphuric acid (p. 286). Under the action of the acid the metal very rapidly becomes covered with a firm layer of sulphate, which protects the underlying metal.

Lead sulphate is appreciably soluble in concentrated sulphuric acid, and crude sulphuric acid almost always contains a large amount of lead. Whether this is due to the formation of acid sulphate, $PbH_2(SO_4)_2$, or whether sulphuric acid is a solvent for lead sulphate as such, has not yet been decided. On diluting with water, the lead sulphate is again precipitated, since, owing to the presence of sulphanion, it is still less soluble in dilute sulphuric acid than in pure water.

* This behaviour, viz. that the solubility of a salt in water is first diminished and then increased by the addition of its acid, is fairly general. The diminution is a regular phenomenon; it is due, as has just been said, to the presence of the anion by reason of which the solubility product is reached even at a much smaller concentration of the cation (by which the solubility of the salt is here measured). The frequently occurring increase of the solubility in very concentrated acid has generally its cause in the formation of a new soluble compound between acid and salt.

On account of its difficult solubility, lead sulphate is used for the separation of plumbion from its solutions in qualitative and quantitative analysis. In order that nothing may be lost in the washing, the sulphate is first washed with dilute sulphuric acid, and this is then displaced by alcohol, in which the sulphate is much less soluble than in water.

Lead Chromate.—On mixing solutions containing chromanion and plumbion, a yellow precipitate of lead chromate is produced, which is very difficultly soluble in water, and which, on account of its strong colour, is used as a pigment under the name chrome yellow. When mixed with Prussian blue, chrome yellow gives a fine green colour called "green cinnabar." Basic lead chromate has a yellowish-red to vermillion-red colour, and is also used as a pigment under the name *chrome orange* and *chrome red.*

The same precipitate of normal lead chromate is also obtained by using a solution of a *dichromate* as the precipitant; hydrion is thereby produced, and the solution reacts acid. The details of this process are exactly the same as in the case of the precipitation of barium salts with dichromates (p. 606). If the anion of the lead salt is that of a strong acid, the precipitation under these conditions remains incomplete, since the hydrion formed reduces the concentration of the chromanion and increases that of dichromanion to such an extent that the solubility product of lead chromate is no longer reached. If, however, the lead salt of a weak acid is employed, *e.g.* lead acetate, precipitation is practically complete, because the hydrion produced is for the most part converted into undissociated acetic acid.

Lead chromate dissolves in strong bases with formation of a yellow liquid. Since chromanion is contained in this, the plumbion must have also disappeared, as otherwise, solution would be impossible. As a matter of fact, the cation, $Pb^{\cdot\cdot}$, is converted into the anion PbO_2'' (p. 646) under the influence of the large amount of hydroxidion present: $Pb^{\cdot\cdot} + 4OH' = PbO_2'' + 2H_2O$.

* This behaviour is evidently a general one; all hydroxides which, like lead hydroxide, possess both basic and acid properties, must exhibit the same reaction, *i.e.* the difficultly soluble salts which they form with any acids are dissolved by alkalis. This is, as a matter of fact, the case; thus, the difficultly soluble salts of alumina, such as the phosphate, dissolve readily in a solution of caustic potash.

Besides being used as a dye, lead chromate is also employed in the laboratory, similarly to copper oxide, as an oxidising agent in the elementary analysis of organic substances.

Lead Acetate, $Pb(C_2O_2H_3)_2 3H_2O$, or *sugar of lead* (so called from its sweet taste), is, of all the lead salts, the one most used in the arts, since it is readily soluble, and therefore allows of the employment of plumbion where necessary. It is obtained by the action of crude acetic acid on lead oxide, the salt being purified by crystallisation.

Lead acetate is very readily soluble in water; its solutions are generally slightly turbid owing to the presence of a white precipitate. The latter consists of lead carbonate, which is formed by the action of the carbonic acid in the air on the salt; this action is facilitated by the volatility of acetic acid.

* If carbon dioxide is passed into a solution of lead acetate, lead carbonate is immediately deposited as a white, crystalline precipitate. The reaction is, however, not complete, and an equilibrium is finally produced in the solution between the remaining plumbion, acetanion, carbanion, hydrion, and the undissociated substances produced from these ions. No carbonate is precipitated by carbon dioxide from the lead salts of strong acids, *e.g.* lead nitrate, nor from the acetate if sufficient acetic acid has been added at the commencement.

* The relations obtaining here are fairly similar to those found in the precipitation of the zinc salts by sulphuretted hydrogen (p. 623),

only that in this case a much smaller concentration of hydrion is sufficient for equilibrium.

Lead oxide dissolves abundantly in solutions of normal lead acetate, and forms basic salts, several of which, *e.g.* $Pb(C_2O_2H_3)(OH)$, have been prepared in the solid state. The solutions are called *vinegar of lead*, and are employed in medicine and as a reagent in the laboratory. They contain appreciable amounts of hydroxidion, for they react alkaline to vegetable colours.

Lead Carbonate, $PbCO_3$, can be obtained as a white precipitate from solutions in which the ions $Pb^{\cdot\cdot}$ and CO_3'' come together. Like magnesium, lead has, although in a less pronounced degree, the tendency to form basic carbonates. In nature the normal carbonate is found in the rhombic forms of aragonite, with which it is isomorphous, and is called *white lead* or *cerussite*.

White lead, the white pigment most largely employed, is a mixture of various basic carbonates. It is obtained by allowing carbon dioxide to act on lead oxide; to facilitate the reaction, acetic acid is generally used as an auxiliary substance. According to the older Dutch process, spirally rolled lead plates were placed in pots in which there was a little vinegar, and were covered with dung which yields the carbon dioxide by its slow oxidation in the air. In these circumstances, the lead plates become covered with a layer of basic carbonate which is shaken off from time to time. At present, it is usual to triturate litharge with some lead acetate and water, and to pass carbon dioxide (obtained by heating limestone) over the mixture. Further, a solution of basic acetate can be prepared from lead acetate and litharge, and this be decomposed with carbon dioxide. In this way, normal carbonate is precipitated, while acetic acid, along with some lead acetate, is left in solution. The liquid is again used to dissolve lead oxide, and so on. As can be seen, the same reactions which here occur separately took place also in the first process side by side.

* Lead acetate here plays the rôle of a catalyser by accelerating the combination of carbon dioxide and lead oxide, a combination which would take place without its presence, only too slowly for manufacturing purposes. In the present case the cause of the acceleration can be recognised to some extent, since by means of the acetic acid the lead oxide is converted into the dissolved condition in which it can more readily unite with the carbon dioxide.

In other words, the velocity of the action of acetic acid on lead oxide, and the precipitation of the carbonate by carbon dioxide, are together much greater than the velocity of direct combination of lead oxide with carbon dioxide. It is probable that it will be possible to attribute many cases of catalytic action to such causes.

* The characteristic of this explanation is that in place of the direct reaction, a series of intermediate reactions occur, which lead to the same final result as the direct reaction. *If these intermediat*

reactions occur more rapidly than the direct reaction, the explanation of the catalytic accelerating action of the intermediate substance is given. Through overlooking the most essential part of this explanation, however, one has become accustomed to see an "explanation" of catalytic accelerations in the mere *possibility* of such intermediate reactions, without thinking of the necessity of proving that these intermediate reactions must proceed more rapidly than the direct reaction, if the entire process is to be accelerated.

Lead Sulphide.—From solutions containing plumbion, sulphuretted hydrogen, even in the presence of hydrion (if this is not too concentrated) precipitates brown-black lead sulphide. Concentrated acid prevents the precipitation, or re-dissolves the precipitated sulphide. We are again dealing here with one of the equilibria which have been repeatedly discussed, and which in this case is characterised by a very slight solubility of the sulphide, and therefore a considerable lack of sensitiveness to hydrion.

This solubility is so small that even the small amount of plumbion contained in the complex salts is sufficient to exceed the solubility product on passing in sulphuretted hydrogen. For this reason, all lead salts, even the complex ones, are precipitated by sulphuretted hydrogen.

Nitric acid oxidises lead sulphide to sulphate.

In nature, lead sulphide occurs in the form of regular cubes with a grey metallic lustre. It is a soft mineral of great density (7·5), which is widely distributed and is called *galena*. This is the most important lead ore.

Compounds of Tetravalent Lead.—As in the case of copper, where the salts of the monovalent type were known only in the solid state, since monocuprion immediately underwent transformation in solution, so, similarly, there is a series of lead compounds which can be referred to tetravalent plumbion, $Pb^{····}$, although this ion does not occur to any considerable extent in solution. The reason of the instability of such salts is, however, to be found in another direction; it has to be sought for in the fact that the anhydride of the tetravalent hydroxide ($PbO_2 = Pb(OH)_4 - 2H_2O$) is a particularly stable and difficultly soluble compound which, with the co-operation of water, is always formed in cases where the tetravalent ion $Pb^{····}$ might be expected. The hydrolytic reaction, $Pb^{····} + 2H_2O = PbO_2 + 4H^{·}$, therefore takes place, *i.e.* lead peroxide and free acid are formed.

Lead peroxide, PbO_2, is a brown substance which has, in the crystalline condition, an almost metallic lustre; it is practically insoluble in water, and is always formed when lead compounds are subjected to powerful oxidising actions. It is generally prepared by the action of bleaching powder on lead chloride in alkaline solution; it is used in considerable quantities as an oxidising agent in the chemical industries.

On being carefully heated in the air, lead oxide also undergoes oxidation, not, however, to the peroxide but to a compound of that with lead oxide: $2PbO + PbO_2 = Pb_3O_4$. The product is a powder of a bright red colour, which has been known for a long time, and is employed as a pigment; it is called *minium* or *red lead.*

* From this name is derived the designation miniature for the ornamental designs on manuscripts, because of the use of this pigment (or of cinnabar, which was formerly confused with it) for that purpose. At the present day, the word has another signification, which has but a slight connection with the original one.

On treating minium with dilute acids which form soluble lead salts, *e.g.* nitric acid, lead nitrate passes into solution, and lead peroxide remains behind as a brown powder: $Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2$. In this way lead peroxide was formerly chiefly obtained.

Another and very important method of preparing lead peroxide is by the conversion of lead salts, *e.g.* of lead sulphate in dilute sulphuric acid, by means of the electric current at the anode. By means of the current, sulphanion, SO_4'', is brought to the anode and discharged, and there occurs the reaction $PbSO_4 + SO_4 + 2H_2O = PbO_2 + 2H_2SO_4$. In accordance with what was stated above, it can be assumed that there first occurs the reaction $PbSO_4 + SO_4 = Pb(SO_4)_2$, the sulphate of tetravalent lead being formed; this is hydrolytically dissociated by the water and passes into lead tetrahydroxide and sulphuric acid, or lead peroxide and sulphuric acid, according to the equation $Pb(SO_4)_2 + 2H_2O = PbO_2 + 2H_2SO_4$. These reactions are of great importance for the construction of electrical accumulators, and will presently be considered more in detail.

If lead peroxide is treated with anhydrous or only slightly hydrated acids, with which therefore hydrolysis is excluded, the corresponding saline derivatives can be obtained. Thus, lead peroxide dissolves in fuming hydrochloric acid in the cold to a dark-coloured liquid from which, by the addition of ammonium chloride, a yellow ammonium salt of hydrochloroplumbic acid, $(NH_4)_2PbCl_6$, is obtained; on decomposing this with concentrated sulphuric acid the acid H_2PbCl_6 is formed, which immediately decomposes into hydrogen chloride and lead tetrachloride, $PbCl_4$. The tetrachloride is found to be a yellow liquid which does not solidify till $-15°$, and which readily decomposes into lead chloride and chlorine. When dissolved in much water it undergoes the above-mentioned hydrolytic dissociation into hydrochloric acid and lead peroxide: $PbCl_4 + 2H_2O = PbO_2 + 4HCl$.

The sulphate and acetate of tetravalent lead can also be prepared under suitable conditions; they are yellow salts which are coloured brown by water owing to the separation of peroxide.

The hypothetical lead tetrahydroxide can also act as an acid, the hydrogen of the hydroxyl being split off as ion. As can be seen from the formula H_4PbO_4 and that of its first anhydride, H_2PbO_3, a tetravalent as well as a divalent acid can be derived from the tetrahydroxide. Minium can be regarded as the lead salt of the tetrabasic acid, for if we replace the 4H by 2Pb we obtain $Pb_2PbO_4 = Pb_3O_4$, the formula of minium. The decomposition of the latter also by means of dilute acids speaks in favour of this view; acids first effect the formation of the free plumbic acid which decomposes into water and the anhydride, lead peroxide.

Another compound of the tetrabasic acid is that with lime, which is formed by heating a mixture of lead oxide and lime in the air, whereby oxygen is taken up. On being heated in carbon dioxide, the salt is decomposed into calcium carbonate, lead oxide, and *oxygen*; on being heated in the air the carbon dioxide again escapes, oxygen is again absorbed, and calcium plumbate is formed. A commercial method of obtaining pure oxygen has been based on these transformations.

The alkali metals, on the other hand, yield salts of the dibasic acid. Lead peroxide dissolves in a strong solution of caustic potash, and from the solution the salt $K_2PbO_3 + 3H_2O$ can be obtained in the crystalline condition. In the solution which contains excess of caustic potash, the presence of the tetravalent ion PbO_4'''' may also be assumed.

The Lead Accumulator.—If two lead plates, one of which is covered with lead peroxide, are placed in dilute sulphuric acid, an effective voltaic cell is obtained the potential of which is 2·0 volts, and which can yield a strong current. The chemical process taking place in this cell consists, on the one hand, of metallic lead being converted into lead sulphate, just as the zinc of the Daniell cell is converted into zinc sulphate, only that in this case the lead sulphate, on account of its difficult solubility, forms a firm layer on the electrode. On the other hand, the lead peroxide is reduced from the tetravalent stage to the divalent, and also forms lead sulphate with the sulphuric acid present. The reaction which yields the energy for the current is therefore represented by the equation

$$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O.$$

The remarkable thing about this cell is that it can be easily reversed. That is to say, if a current is passed through the cell in the opposite direction, the sulphate is at the one pole reduced to metallic lead, and at the other oxidised to lead peroxide (p. 652). The cell, therefore, again passes into its former condition, and can again yield a current.

At first sight, this appears a fact of very small importance. For according to the law of the conservation of energy there can be obtained from the charged cell only as much electrical energy as was used up in the charging; in all circumstances, therefore, there is no gain, and indeed, in consideration of the unavoidable losses, there is even a profitless consumption of electrical energy. This is certainly the case; the advantage, however, which lies in the possibility of storing comparatively large quantities of electrical energy in a small weight, and of rendering any portion of it available for use whenever desired, is so great that the above-mentioned loss is willingly accepted. Consider, for example, a factory in which large amounts of electrical energy are required from time to time, while in the intervals little is necessary; the dynamo would then have to be large enough to supply the powerful currents without being damaged, while in the intervals it would have to run empty. If, however, an *electrical accumulator* were connected with the plant, the dynamo would have to be constructed only for the average consumption and not for the maximal, since during the time of large consumption the accumulator would yield energy, while in the intervals of small consumption the accumulator would take up the energy of the dynamo and retain it for use when required.

This result would be obtained by inserting a voltaic cell which can act in the double manner, *i.e.* which can on the one hand yield a current, and, on the other, can store, by means of the reverse chemical reaction, the current of opposite direction. This property is possessed by many cells, *e.g.* the Daniell, in which, by the reverse current, zinc is deposited and copper dissolved, copper sulphate therefore being formed.

Hitherto, however, the lead accumulator which has just been described is the only one which has proved to possess vitality, since it has the advantage of containing *only one metal.* This is rendered possible by the circumstance that the metallically conducting lead peroxide is a very strong oxidising agent, while the metallic lead acts as a (moderate) reducing agent. In the cells of the type of the Daniell, which contain two metals, one cannot, in the long run, prevent the solution of the one metal (copper) passing into that of the other (zinc), whereby instead of the indirect chemical process, which yields the current, the direct process occurs, which only yields heat, and the cell therefore no longer acts.

A lead accumulator, therefore, consists of two lead plates placed in dilute sulphuric acid. In order that as large an amount of electrical energy as possible may be absorbed for a given weight of the accumulator, the plates are made porous, so that the acid has as far as possible access to every part. To combine this requirement with the greatest possible durability of the plates, is the real problem of the electrical accumulator. The problem is generally solved by filling up a lead grating with spongy lead, obtained by the electrical reduction of various lead compounds. Such a plate of spongy lead is then connected with a second plate, in which the spongy lead has been converted into lead peroxide by electrical oxidation. Such plates are prepared, for example, by filling in the lead grid with a mixture of lead oxide and sulphuric acid in the form of a thick paste, suspending two such plates, after the paste has solidified, in dilute sulphuric acid, and passing a current through it. On the one side the lead sulphate present is then reduced to metallic lead, and on the other oxidised to peroxide. The end of the transformation can be recognised in the evolution of hydrogen at the former plate and of oxygen at the latter; at the same time, the potential of the current necessary for charging rises. The accumulator is then charged. When, after the charge has been withdrawn, the accumulator has to be recharged, care has to be taken that the former peroxide plate is again used for the same transformation, as otherwise the plates will be destroyed.

As can be seen from the equation of the reaction given on p. 653, sulphuric acid passes into combination while the accumulator is in action, and is again set free when the cell is charged. In the amount of sulphuric acid in the accumulator, therefore, we have a measure of the condition of charging, and as the density also changes with the amount of acid, a hydrometer floating in the liquid allows of the condition as to charge being easily determined. This is of importance, since experience has shown that an accumulator deteriorates on standing for a lengthened period in the uncharged condition, because the lead sulphate in the plates partially loses its chemical reactivity.

Metallurgy of Lead.—For the manufacture of lead, galena is the only ore which has to be considered in practice. This is first roasted, whereby a part of the sulphur escapes as sulphur dioxide, while another portion remains behind in the roasted mass, the lead sulphide being converted into lead sulphate. The mixture of lead oxide, lead sulphate, and unchanged lead sulphide is then fused with exclusion of air, whereby the following reactions occur:—

$$PbS + 2PbO = 3Pb + SO_2$$
$$PbS + PbSO_4 = 2Pb + 2SO_2.$$

In this particular case, therefore, the unchanged lead sulphide acts as a reducing agent on the oxygenated products formed, and the result is metallic lead along with sulphur dioxide.

The "work lead" thus obtained generally contains silver, to obtain which it is further treated; the processes for this will be discussed under silver.

CHAPTER XXXIV

MERCURY

General.—In its chemical relations, mercury is most nearly allied to copper, since it forms, like it, two elementary ions, a monovalent and a divalent, which in many respects also are similar to those of copper. With cadmium it shares the tendency to form slightly dissociated halogen compounds of the divalent series.

Metallic mercury occurs free in nature, and by reason of its being liquid at medium temperatures, it has attracted attention from remote times. In the older history of chemistry, while the experimental conception of a chemical element was not yet developed, mercury was regarded as the type of the metallic character; this found expression in the fact that mercury was regarded as a constituent of all metals. The endeavours to prepare gold and silver from base metals, which are connected with this view, had generally for the first purpose, the "fixing" of the mercury, *i.e.* making it non-volatile. For this reason, and through the discovery made about the fifteenth century of the powerful medicinal actions of the mercury preparations, the chemistry of mercury became known at an earlier period than that of most of the other metals.

During the development of the newer period of chemistry at the end of the eighteenth century, mercury again played a considerable rôle. This was due, in the first place, to the chemical properties of mercury oxide. The possibility of converting the metal into its oxide by heating in the air, and of effecting the separation of this into metal and oxygen by more strongly heating, was of the greatest importance for the correct interpretation of the phenomena of oxidation (p. 37). On the other hand, the introduction of the mercury pneumatic trough for the investigation of gases, at once led to the discovery of a series of hitherto unknown substances (p. 179).

Up to the present day, mercury has not lost its importance for scientific investigation. Its liquid nature, fairly great chemical resistibility, considerable density, etc., assure its unceasing use for physico-chemical apparatus, of which the thermometer and barometer need only be mentioned as the most important. Since, being a liquid metal, it is not subject to the variations which are exhibited by the solid metals in consequence of being wrought, it is employed as a standard metal for electro-chemical apparatus, and many other scientific applications could also be mentioned.

Metallic mercury has the density 13·595 at 0°. Its expansion by heat is, up to the boiling point of water, so nearly proportional to that of the gases that the mercury thermometer agrees well with the gas thermometer over this range. At − 39·4°, mercury solidifies to a silver-like solid metal; it thereby readily exhibits in a considerable degree the phenomena of supercooling (p. 116). At 358°, mercury boils under the pressure of the atmosphere. Since, in many measurements, the vapour pressure of mercury at comparatively low temperatures also comes into account, we give the following table of vapour pressures :—

0°	0·00002 cm.	150°	0·29 cm.
20°	0·00013 ,,	200°	1·82 ,,
40°	0·0007 ,,	250°	7·58 ,,
60°	0·0028 ,,	300°	24·2 ,,
80°	0·0093 ,,	350°	66·3 ,,
100°	0·0280 ,,		

From this it is seen that up to 100°, the vapour pressure is small, viz. less than 1 mm.

In the air, mercury behaves in general as a "noble" metal, *i.e.* it does not oxidise spontaneously. This is not, however, in all strictness the case, for if it is maintained for a lengthened period at about 300°, it slowly becomes covered with red crystals of mercury oxide. Water, standing in contact with mercury, assumes poisonous properties. Whether this is due to the solution of a trace of oxide formed, or to the solution of metal in water, has not yet been determined.[1]

The combining weight of mercury has been found by analysis of the oxide and sulphide to be Hg = 200·3. The vapour density shows the molar weight to be 200; the two are therefore equal. On account of its low boiling point, mercury was the first metal in the case of which this remarkable relation was established (p. 470).

Pure mercury does not wet glass; if, however, it contains foreign metals dissolved in it, it becomes covered with a film of oxide, the effect of which is that the metal no longer flows over glass and other urfaces in round drops, but "leaves a tail." This is a very sensitive est of the purity of the metal.

* In order to purify mercury, a task which is constantly occurring

in the laboratory, it is shaken with dilute sulphuric acid, to which from time to time some drops of potassium dichromate are added; it is then washed with a large quantity of water and dried by gently heating it. In this way, considerable impurities can be quickly removed. The fairly pure metal is allowed to flow in small drops through the apparatus shown in Fig. 116, which is filled with a dilute acid solution of mercurous nitrate (*vide infra*). These methods depend on the fact that the oxidising agents employed oxidise the contaminating metals rather than the mercury; in order that the object may be attained, fine division is necessary.

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[1] That metallic mercury can dissolve in water, must be regarded as indubitable. or, all gases dissolve in water; since mercury has an appreciable, although small, vapour ressure even at room temperature, its vapour must also be soluble in water. There is, owever, no difference between a solution of liquid and one of vaporous mercury, since in le case of a solution only the existing state is of importance and not the former states of s components.

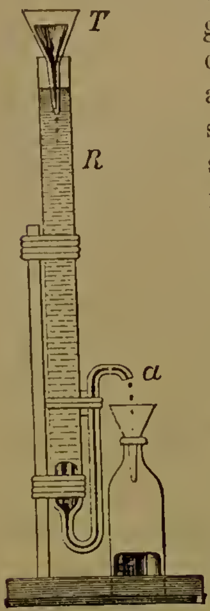

FIG. 116.

Mercury Ions.—Mercury forms two elementary ions: monomercurion, $Hg^{\cdot}$, and dimercurion, $Hg^{\cdot\cdot}$. In its properties the former is allied to monocuprion and argention; the latter does not exhibit any very close relations to other metals. In comparatively concentrated solutions monomercurion perhaps occurs as the divalent double ion of the formula $Hg_2^{\cdot\cdot}$; in very dilute solutions, as monovalent $Hg^{\cdot}$. For the sake of clearness, and until the corresponding relations have been explained in the case of the other monovalent ions of the heavy metals, we shall use the simple method of writing the formulæ, especially as it does not conflict with any experimental fact to be discussed here.

Monomercurion is formed when salts of mercury are prepared in presence of an excess of metallic mercury. The most convenient solvent for mercury is dilute nitric acid; if too great a concentration of nitric acid and too high a temperature are avoided, mercurous nitrate is formed with evolution of nitric oxide (p. 322). If, owing to the causes just mentioned, mercuric nitrate has been formed, it is sufficient to allow the solution to stand for some time over metallic mercury in order to again convert it into mercurous salt. The reaction $Hg^{\cdot\cdot} + Hg = 2Hg^{\cdot}$ then takes place almost completely.

In the absence of metallic mercury, however, monomercurion is readily oxidised to dimercurion.

The solutions of the two ions cannot be distinguished by thei appearance, since they are both colourless. Their compounds, how-ever, with the same anion have frequently very different solubility and they can be distinguished by this means.

The two ions are violent poisons both for the higher and the lowe organisms. Since, however, monomercurion forms a very difficultl soluble compound with the chloridion occurring everywhere in th organism, whereby its concentration and therefore its action is re-duced to exceedingly small values, mercury poisoning occurs, as matter of fact, almost exclusively by means of dimercurion.

Mercurous Compounds.—From the solutions of mercurous salts, black mercurous oxide, Hg_2O, is precipitated by bases. The mercurous hydroxide, the formation of which might be expected, is so unstable that it has not been possible to detect it with certainty; on its formation, it apparently passes immediately into its anhydride. Mercurous oxide is a black, unstable powder which on being kept for some time is converted into mercuric oxide and metallic mercury: $Hg_2O = HgO + Hg$; in sunlight the conversion is rapid.

The basic properties of this oxide are only feebly developed, for the mercurous salts, so far as they are soluble in water, undergo hydrolysis with formation of precipitates of difficultly soluble basic salts. In order to obtain clear solutions, excess of free acid must be added.

This holds, for example, in the case of *mercurous nitrate*, $HgNO_3$, which is readily obtained by dissolving mercury in dilute nitric acid. In the cold, the salt crystallises from the solution containing excess of acid; on attempting, however, to re-dissolve it in water, a white precipitate of basic nitrate is deposited, the amount of which is all the greater the greater the amount of water compared with that of the salt. The solution can be again made clear by the addition of nitric acid, and there is a definite concentration of free acid, varying with the temperature, at which no decomposition of the salt occurs.

Mercurous Sulphate, Hg_2SO_4, is a salt, very difficultly soluble in water, which is formed by warming mercury with concentrated sulphuric acid. Half of the sulphuric acid then acts as an oxidising agent, and passes into sulphur dioxide and water; the other half of the acid yields mercurous sulphate, which is deposited as a white, coarsely crystalline powder. If the excess of sulphuric acid is removed by washing with water, hydrolysis commences after the main portion of the acid has been removed, and the salt becomes dark in colour.

Mercurous sulphate is used as the initial substance in the preparation of other mercury compounds, and for the construction of electrical standard cells.

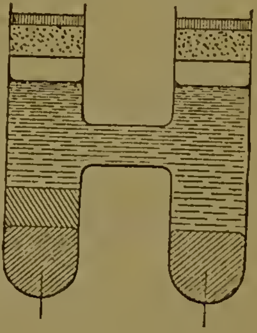

FIG. 117.

* Such standard cells serve the purpose of furnishing at all times a definite value of electrical potential for the purposes of measurement. The most largely employed of these cells is represented in Fig. 117. In the one limb there is contained mercury covered with mercurous sulphate, and in the other there is a 12 per cent mixture of cadmium and mercury; the remaining space is occupied with a saturated solution of cadmium sulphate, to which some crystallised cadmium sulphate has been added. The potential of such a cell amounts to 1·0186 volt; by using fairly pure substances, the same potential is always obtained to within a ten-thousandth of its value, and changes only slightly with the temperature.

Mercurous Chloride, HgCl, is a white salt, soluble with extreme difficulty in water, and has long been employed in medicine under the name calomel. By reason of its small solubility it passes only slowly into the system, and therefore exhibits correspondingly mild actions. Its application in medicine depends on this.

Calomel is obtained on bringing together a soluble mercurous salt with chloridion; thus mercurous salts are precipitated not only by solutions of normal chlorides, but also just as completely by hydrochloric acid. This behaviour could be foreseen, for the solubility of difficultly soluble salts in acids depends, indeed, on the fact that their anions can form undissociated compounds with the hydrion of the acid added, so that the concentration of the anion is diminished, and the solubility product thereby not attained. In the present case this cannot happen, because the anion of calomel, viz. chloridion, is that of one of the strongest acids, and is therefore not converted to any considerable extent into the undissociated condition even by the addition of hydrion. For this reason the solubility product of a calomel solution also remains essentially unchanged on the addition of a strong acid, and no more passes into solution.

On treating calomel with a *concentrated* solution of sodium chloride or hydrochloric acid, however, a quite appreciable amount of it passes into solution; at the same time some mercury is deposited. This reaction will be explained in the case of the iodine compound, in which it is much more distinct.

Mercurous sulphate also is converted into calomel on being treated with a solution of sodium chloride or hydrochloric acid, because the latter is far more difficultly soluble. As a rule, however, it is obtained from the sulphate by subliming it with common salt, whereby the calomel is obtained in semi-transparent crystalline masses with a diamond lustre (on account of its high index of refraction). Since, ordinarily, more or less mercuric chloride is mixed with it, calomel, which is to be used for medicinal purposes, must be previously carefully extracted with water in order to remove the very poisonous, soluble mercuric chloride.

* Calomel readily volatilises, and its vapour density was therefore early determined. This yields the molar weight 235, corresponding to the simple formula HgCl. Since mercury was regarded as being always divalent, this result stood in conflict with a former, specially favoured assumption, according to which the different elements possess a definite, unchangeable valency; the double formula Hg_2Cl_2, however, could be brought into agreement with the divalency of mercury, according to the formulation $ClHg - HgCl$. A lively discussion therefore arose as to whether the vapour of calomel is uniform or has decomposed into mercuric chloride and mercury, according to the equation $Hg_2Cl_2 = HgCl_2 + Hg$. An unequivocal decision of this point, supported by numerical data, has not yet been effected.

Mercurous bromide and iodide are similar to calomel. The iodide is a greenish powder, which is most easily obtained by rubbing iodine and mercury together in the proportions of their combining weights, and which decomposes with extreme readiness into mercuric iodide and free mercury.

Mercuric Salts are obtained from the mercurous compounds by subjecting these to oxidising actions. Thus, mercuric nitrate, $Hg(NO_3)_2$, is formed on dissolving mercury in concentrated and warm nitric acid, and can be obtained in colourless crystals on evaporating the solution. In the same way mercurous sulphate, on being heated with an excess of sulphuric acid, passes into the mercuric salt with renewed evolution of sulphur dioxide: $Hg_2SO_4 + H_2SO_4 = 2HgSO_4 + SO_2 + H_2O$.

The mercuric salts exhibit the property of hydrolysis in a much higher degree than those of the mercurous series. Since in this case the basic salts are characterised by a yellow colour, the occurrence of the decomposition can be readily recognised. Nevertheless, a number of salts of the mercuric type are known, which can be dissolved in water without sign of decomposition; this is due to special properties, which will be discussed immediately.

Mercuric oxide, HgO, is obtained from the mercuric salts by means of soluble bases. The hydroxide is not known; it may therefore be again assumed that it is indeed first formed, but that it immediately passes into its anhydride.

Mercuric oxide is a yellow to red powder, the colour of which depends on the fineness of its division. If it is precipitated from cold solutions it appears yellow; when precipitated hot an orange-coloured precipitate is formed. It is obtained as a red crystalline powder by heating mercurous or mercuric nitrate to a moderate temperature; nitrogen peroxide and oxygen escape (cf. p. 647), and mercuric oxide remains behind. The decomposition can easily be made complete without the temperature being reached at which the oxide decomposes into the metal and oxygen.

As has been repeatedly mentioned, mercuric oxide is also produced directly from mercury and oxygen by allowing the two to act on one another at about 300°. The reaction is, however, very slow. In this case a condition of equilibrium, depending on the temperature, is established between mercury, oxygen, and mercuric oxide. According to the temperature and pressure of the oxygen the reaction can be made to take place in one or other direction.

The preparation of *mercuric nitrate* has been already given. The basic nitrate which is precipitated from the salts by water has the composition $Hg_3(NO_3)_2(OH)_4$. It readily dissolves in hydrochloric acid, forming a clear solution.

The same holds for *mercuric sulphate*, $HgSO_4$. The basic salt, which is obtained as a yellow crystalline precipitate on treating the normal salt with water, has a corresponding composition,

$Hg_3SO_4(OH)_4$, and under the name "turpeth mineral" is applied in medicine.

The behaviour of the halogen compounds is in marked contrast to that of the mercuric salts of the oxyacids. So far as they are soluble they dissolve in water without appreciable hydrolysis, and exhibit nothing of the ready decomposability of the above salts.

The explanation is found on determining the electrical conductivity of the solutions of these substances. This is found to be very slight, and it follows from this that we are here dealing with salts which, unlike the preponderating majority of such substances, are not greatly dissociated into ions; they can exhibit the reactions of the ions, therefore, only in a very limited degree.

The one which is most dissociated is the chloride, $HgCl_2$. This chlorine compound of mercury has also been known for a very long time. On account of its poisonous properties and its method of preparation (by the sublimation of mercuric salts, especially the sulphate, with sodium chloride) it is called corrosive sublimate.

Mercuric chloride is a colourless, crystalline salt, which is moderately soluble in water; it has a considerable density (7·2), and its solutions have been found to be a very violent poison for higher as well as lower organisms. It is therefore extensively used in medicine as a disinfectant, *i.e.* for the purpose of killing the spores of harmful schizomycetes, and such like, and its use is limited only by the fact that it is also a powerful poison for the human organism. Small quantities of it exercise a specific, medicinal action.

At 265° mercuric chloride melts, and boils at 307°, so that it can be readily volatilised, and thereby purified. Its vapour density yields the molar weight 271, corresponding to the formula $HgCl_2$.

* The solutions of mercuric chloride are fairly easily reduced to calomel. Of these reductions, that with oxalic acid (p. 410) is of particular interest, as it takes place with measurable velocity only in light, while in the darkness it remains practically at a stand-still. This reaction has therefore been used as a means of measuring the chemical action of light or as a chemical photometer. It is represented by the equation $2HgCl_2 + C_2O_4H_2 = 2HgCl + 2CO_2 + 2HCl$. Carbon dioxide and hydrochloric acid are therefore formed in the reaction; to counteract the action of the latter one of the salts of oxalic acid, *e.g.* ammonium oxalate, is used instead of the free acid. The indications of this photometer are also only individual (p. 583).

From its solutions mercuric oxide is precipitated by soluble, strong bases, but on quantitative investigation it is found that the amount of oxide precipitated never corresponds to the amount of base taken, but is less. Conversely, mercuric oxide dissolves in solutions of other chlorides, and liquids are produced with a strongly alkaline reaction. This is due to the fact that the solution of mercuric chloride contains only very little dimercurion. On adding a base, *i.e.* hydroxidion, there must be a definite, finite concentration of the latter before the solubility product of the mercuric oxide is reached and that substance precipitated. On the other hand, when chloridion is added to an aqueous solution of mercuric oxide (in which the presence of dimercurion and hydroxidion must be assumed), the greater part of the dimercurion present is converted into undissociated mercuric chloride, and more mercuric oxide must pass into solution in order that the solubility product may be again established. This process is repeated, and when equilibrium is finally reached there is an appreciable amount of hydroxidion, from the mercuric oxide, present in the solution.

Mercuric chloride is extremely stable to concentrated sulphuric acid, and even on heating not the slightest evolution of hydrogen chloride occurs. Nor is it acted on by concentrated nitric acid, which attacks all other saline chlorides with evolution of chlorine or nitrosyl chloride (p. 335). The behaviour in both cases is due to the very slight electrolytic dissociation of mercuric chloride.

Mercuric chloride crystallises along with the alkali chlorides, forming compounds which appear to occupy a position intermediate between the ordinary double salts, the components of which exist side by side in solution, and the complex salts, the ions of which are formed by the union of the one salt with the ion of the other; that is to say, the salts partly exist side by side in solution, and are partly combined in the above complex compounds, and the relative quantities of the two depend on the temperature and the concentration.

* Strictly speaking, such a view holds for all double salts and complex salts, and the two are distinguished from one another only by the fact that the one or the other greatly predominates. In the case of the above mercury compounds we have apparently the case, which otherwise does not frequently occur, that the two portions are present in about equal amounts.

The complex salts, whose presence can here be assumed, are the alkali salts of the mercurichloride ions $HgCl_3'$ and $HgCl_4''$. From the solutions of the mixed single salts compounds of the one or other type, *e.g.* $KHgCl_3$ and K_2HgCl_4, are obtained, according to the concentration and the temperature, and we must therefore regard both as being present together in solution. If for any reason one or other of these compounds separates out, the equilibrium in the solution is disturbed; the compound is again formed at the expense of the substance present, and so on. A more thorough investigation of the conditions of equilibrium has still to be carried out.

* The above relations are of importance for the application of corrosive sublimate for purposes of disinfection. It has been found that the poisonous action of the mercury salts is proportional to the concentration of the dimercurion present. By the addition of alkali chlorides, now, the concentration of the dimercurion is certainly diminished; either by the formation of the above mentioned complex

ions or by the diminution of the dissociation in consequence of the mass action of the chloridion. The addition, therefore, of sodium chloride to corrosive sublimate, which is frequently made, always causes a diminution of the poisonous action as compared with a solution of pure sublimate containing an equal amount of mercury, and where necessary one must be aware of this influence in order not to make mistakes in estimating the disinfecting power of a given solution.

The formation of the corresponding hydrochloromercuric acid can be recognised on treating mercuric chloride with concentrated hydrochloric acid. Considerable amounts of that salt then pass into solution with a remarkable rise of temperature, and the solution no longer fumes; it therefore contains much less free hydrochloric acid. On cooling the mass solidifies to crystals of the composition $HHgCl_3$.

Mercuric chloride unites with mercuric oxide to form compounds, *oxychlorides*, which have the general formula $m\mathrm{HgCl_2} \cdot n\mathrm{HgO}$, in which the ratio $m : n$ can vary from 6 : 1 to 1 : 2. The various compounds are obtained by treating varying amounts of oxide with more or less concentrated solutions of the chloride at different temperatures. The compounds comparatively rich in oxide are red, brown, or black, some even violet; those rich in chloride are lighter in colour, varying to pale yellow. While the latter give up chloride to water, the former do so only in a very slight degree, so that an aqueous solution of mercuric chloride loses almost all its chloride on being shaken with mercuric oxide. This reaction is made use of in the preparation of hypochlorous acid from chlorine water by means of mercuric oxide.

Mercuric Bromide, $HgBr_2$, is a white, very slightly soluble salt, which is very similar to the chloride, and can be readily obtained from its elements. In all its chemical relationships also it is so closely analogous to the chloride that the preceding description could be repeated almost word for word. Its electrolytic dissociation is still less than that of the chloride, its tendency to form complex compounds greater.

Mercuric Iodide, HgI_2, is a red substance which is only slightly soluble in water (1 : 120), but readily dissolves in alcohol, from which it separates out on evaporation in red quadratic crystals. It is most easily obtained by rubbing mercury and iodine together in the proportions 4 : 5 by weight.

If the substance is heated it becomes yellow above 126°, passing at the same time into another crystalline form; on being kept in the cold it again changes into the red variety. It is therefore an enantiotropic substance, and 126° is the transition temperature which separates the two regions of stability from one another (p. 254).

* If in any way, however, solid mercuric iodide is caused to form at a lower temperature, it is always the yellow form that first appears. This is one of the most striking examples of the rule which has often been mentioned that the unstable forms appear first. This can be

readily observed by precipitating mercuric chloride with a solution of potassium iodide. A bright yellow precipitate is first formed, which in a few moments changes into the red one. The yellow form maintains its existence longer when formed by the precipitation of an alcoholic solution of the salt with water. In consequence of its very fine state of division it is very light yellow, almost white, in colour. The conversion into the stable red form is greatly accelerated by light. When exposed to sunlight the vessel with the light yellow precipitate becomes red in a few minutes on the side turned towards the light.

* Further, when the red salt is volatilised, the vapour always condenses on the colder portions in the yellow form. This occurs, no matter whether the vapour has been generated from the red or the yellow salt, which shows that the distinction between the solid forms does not exist in the vapour.

Mercuric iodide is a very stable compound, which is scarcely attacked by dilute solutions of the ordinary reagents. This is due to the fact that it is even less dissociated into its ions than mercuric chloride is. On the other hand, it is formed with extreme ease from its constituents.

Mercuric iodide forms very stable complex compounds with the odine compounds of the other metals. These will be described later.

The behaviour of *mercuric fluoride* is in striking contrast with the great stability of mercuric chloride, bromide, and iodide. Mercuric oxide, it is true, dissolves in excess of hydrofluoric acid, but on diluting the solution with water a basic salt of a yellow colour is deposited, and f this is treated with further quantities of water pure mercuric oxide remains behind free from fluorine compounds. This is a behaviour peculiar to the oxy-salts of mercury, and shows the considerable deviation of fluorine from the other halogens (p. 241).

Mercuric Sulphide.—While a sulphur compound corresponding to mercurous oxide is not known, the compound HgS, corresponding to mercuric oxide, is a very stable substance which is readily formed, occurs naturally, and has long been known.

* If the solution of a mercurous salt is precipitated with sulphuretted hydrogen, a black precipitate is indeed formed. On investigation, however, this is found to be a mixture of mercuric sulphide and metallic mercury. It can be assumed that the mercurous sulphide first ormed decomposes into these two substances: $Hg_2S = HgS + Hg$.

Mercuric sulphide is obtained as a black powder by triturating the wo components together. It is also obtained by the precipitation of mercuric compounds with sulphuretted hydrogen. In this case it is ndifferent whether the solution reacts acid or neutral, since mercuric ulphide is extremely difficultly soluble, and its precipitation is thereore not appreciably affected by acids. From the other metallic ulphides it is distinguished by the fact that it does not have the east tendency to oxidise in the air. It is a much more stable compound than mercuric sulphate, which could be produced by its oxidation.

In nature mercuric sulphide occurs in comparatively large quantities. It constitutes the most important ore of mercury, and is called *cinnabar*. Pure cinnabar crystallises in red-grey, hexagonal masses with a metallic lustre, and on being ground yields a powder of a fine red colour. It is another form of mercuric sulphide; the black product may be regarded as amorphous.

From the fact that the black form was first produced in the formation of mercuric sulphide, it can be concluded that it is the less stable and the red crystalline form the more stable variety. This follows from the spontaneous transformation of the former into the latter. If a solution of alkali sulphide (in which mercuric sulphide is somewhat soluble) is poured over the black mercuric sulphide red spots are formed after some time in the black mass, and these continue to grow until the whole mass has become red, *i.e.* has become converted into the crystalline form.

* Being the less stable form, the black mercuric sulphide must be more soluble in all solvents than the red. If, therefore, the liquid is saturated in respect of the black form, it is supersaturated in respect of the less soluble red form, and if any of the red form is present, or is produced, a further quantity of the red sulphide must there separate out. The solution thereby becomes unsaturated in respect of the black form, and a further portion of this is dissolved. In this way precipitation and solution are repeated until the unstable form has completely disappeared. Transformations of this kind are therefore generally accelerated by solvents, since these act as intermediaries, whereas otherwise only those portions of the two forms which are in direct contact can influence one another.

On account of its fine colour cinnabar is used as a pigment. It is, however, not very stable to light. The two forms of mercuric sulphide are not appreciably soluble in dilute acids, and nitric acid also is without action on them. They dissolve, however, in aqua regia or other reagents, which evolve free chlorine. This behaviour is due to the slight stability of the oxygen salts of mercury and the great stability of the halogen compounds. This is made use of for the analytical separation of mercury from the other metals, whose sulphur compounds are insoluble in dilute acids, for all the other sulphides of this group are attacked by nitric acid.

* Mercuric sulphide dissolves abundantly in concentrated solutions of the alkali sulphides. On dilution it is again almost completely precipitated in the black form. This phenomenon is due to the formation of a thio-salt, *i.e.* of a saline compound in which sulphur takes the place of oxygen (cf. p. 412). In this respect mercury forms a transition to the metals of the next group, in which this behaviour is general, and in which the corresponding compounds exist even at

great dilution. The new chemical relations which are met with here will be discussed in the case of these other compounds.

On passing sulphuretted hydrogen into solutions of mercuric salts, white precipitates are first produced, which on further action of the sulphuretted hydrogen become yellow, red, and finally black. These are compounds of varying amounts of mercuric sulphide with the mercuric salts present, and are decomposed by sulphuretted hydrogen and converted into the pure sulphide. The behaviour is very characteristic, and can be used for the direct identification of mercury in precipitation with sulphuretted hydrogen.

Mercury sulphide occurs in nature partly in fine crystalline form as cinnabar, partly mixed with other substances, as hepatic cinnabar. From these, metallic mercury is obtained by simply roasting; the sulphur is thereby converted into sulphur dioxide, while the mercury volatilises as the metal. By condensing the vapours, crude mercury is obtained, and is purified mechanically by pressing through chamois leather.

Mercuric Cyanide, $Hg(CN)_2$, is a colourless salt, which is fairly soluble in water but does not exhibit the reactions either of cyanidion or of dimercurion. The conclusion to be drawn from this, viz. that it is not electrolytically dissociated, is confirmed by the fact that its aqueous solution does not conduct the electric current, and that the depression of the freezing point yields the complete molar weight 252, which also shows the absence of dissociation.

As a result of the negligibly small degree of dissociation, the compound is formed in all cases in which the ions cyanidion and dimercurion come together even in very small concentration. Thus, Prussian blue (p. 579), for example, is at once decomposed by boiling with water and mercuric oxide, mercuric cyanide passing into solution, and ferric oxide being deposited. This reaction is also employed for the purpose of obtaining mercuric cyanide.

When it is heated in the solid state, it decomposes into cyanogen gas, which escapes, and mercury, which distils into the colder portions of the apparatus. This decomposition serves as a convenient method of obtaining cyanogen gas (p. 412). In this process a portion of the cyanogen always separates out in the polymerised condition as a black-brown powder of paracyanogen.

If the solution of mercuric cyanide is mixed with that of an alkali cyanide, a considerable evolution of heat occurs, which indicates the formation of a new compound. This can also be obtained in the solid state; the potassium compound has the composition $K_2Hg(CN)_4$, and is the potassium salt of a mercuricyanidion $Hg(CN)_4''$, which is similar in composition to the nickelcyanidion (p. 617).

The corresponding acid $H_2Hg(CN)_4$ is not very stable, but decomposes readily into mercuric cyanide and hydrocyanic acid.

Complex Compounds of Mercury.—As might be expected from the slight dissociation of the halogen compounds of mercury, this metal has a great tendency to form complex compounds the aqueous solutions of which contain dimercurion only in extremely small amount, and in which mercury forms a component of more complex ions or salts. Such complex compounds are met with, on the one hand, in the case of the halogen derivatives; on the other hand, sulphur and nitrogen also have the power of forming many such compounds with mercury. On account of the large number of such substances, these cannot be treated exhaustively here, and the characterisation of the most important types must suffice.

In the first place, the three heavier halogens form such complex compounds, the stability of which increases with the combining weight of the halogens. The most important type represented here is that of the halogenmercuric ions HgA_4'', where A denotes the halogen. It will be sufficient if we describe the relations in the case of the iodine compound, which is the most stable and which, on account of the difficult solubility of mercuric iodide, gives rise to the most readily understood phenomena (cf. p. 663).

Mercuric iodide readily dissolves in aqueous solutions containing iodidion, and it does so all the more abundantly, the more concentrated the solutions. On dilution, mercuric iodide is precipitated, but there always remains in the solution rather more of it than corresponds to the relation $HgI_2 : 2I'$. The solutions are pale yellow in colour, exhibit none of the reactions of mercury, and partly yield the corresponding salts in the solid state on evaporation, *e.g.* the potassium salt K_2HgI_4; they contain the complex anion HgI_4''.

No mercuric oxide is precipitated from their solutions by the addition of strong bases; on the other hand, mercuric oxide dissolves abundantly, for example, in a solution of potassium iodide yielding a solution with a strongly alkaline reaction. In this case the reaction $4KI + HgO + H_2O = K_2HgI_4 + 2KOH$, or writing the ions, $4I' + HgO + H_2O = HgI_4'' + 2OH'$, takes place to a large extent. Such an alkaline solution of potassium mercuric iodide is used under the name of "Nessler's reagent" for the detection of small traces of ammonia. This reaction, which depends on the formation of a new complex compound, will be discussed at a later point.

Bromine and chlorine form complex compounds which are similar but less stable.

* Some apparent contradictions in the behaviour of the mercury compounds can be explained by the formation of these stable, complex compounds. Thus, it was mentioned on p. 658, that dimercurion in contact with metallic mercury passes into monomercurion. If, however, mercurous iodide is treated with potassium iodide, metallic mercury is deposited, and half of the mercury passes as iodide into solution. The reaction is: $2HgI + 2KI = K_2HgI_4 + Hg$. The reaction of the ions is: $2HgI + 2I' = HgI_4'' + Hg$; it is therefore not *dimer-*

curion that is formed but a complex compound (which, according to its state of oxidation, belongs to the mercuric series), and there is therefore no contradiction of the former reaction between the two mercury ions.

* A similar action occurs between potassium bromide and mercurous bromide, and even between the chlorine compounds. The more concentrated the solution of a soluble chloride is, the greater is its solvent action on calomel, mercury being separated out in the metallic state and (undissociated) mercuric chloride passing into solution. On account of the powerful physiological actions of the latter salt, a knowledge of this reaction is of importance in medicine.

* Calomel is of course still much more soluble in potassium iodide and all other liquids containing iodidion.

Complex Ammonia Compounds.—Both series of mercury compounds give rise to the formation of complex compounds with ammonia; only the substances belonging to the mercuric series, however, have been thoroughly investigated. If ammonia is allowed to act on *mercurous* salts, these become black. The reaction has the appearance as if mercurous oxide were precipitated by the base; the black precipitates, however, contain nitrogen, and can be regarded as ammonium salts in which two combining weights of hydrogen are replaced by two combining weights of mercury. Besides this series of compounds, there are, however, other compounds which are formed at the same time as the first series, so that the composition of the black precipitates differs in many respects from the simple scheme. The preparation of the single salts is greatly increased in difficulty by the fact that they are not soluble, and therefore cannot be recrystallised.

* This blackening is used as a characteristic test for ammonia, paper moistened with mercurous nitrate being held in the gas to be investigated. The reaction is, however, less sensitive than that with litmus paper.

The complex ammonium compounds of the mercuric series can also be regarded as ammonium salts in which the hydrogen of the ammonium is replaced by mercury, only that in this case one combining weight of mercury, on account of its divalency, replaces two combining weights of hydrogen. From these considerations we obtain, in the first instance, the following cations:—

Dimercurammonion	$Hg_2N^{\cdot}$
Mercurammonion	$HgH_2N^{\cdot}$
Mercurdiammonion	$HgH_6N_2^{\cdot\cdot}$

In the case of dimercurammonion, all the hydrogen of the ammonium is replaced by mercury; in mercurammonion, only the half, and mercurdiammonion, finally, corresponds to two combining weights of ammonium, which have together lost two hydrogens, these having been replaced by one combining weight of mercury.

The hydroxide corresponding to dimercurammonion is obtained on allowing finely divided mercuric oxide to stand under concentrated ammonia solution. Without apparently any great change taking place—the colour only becomes somewhat lighter—there occurs the reaction, $2HgO + NH_3 = Hg_2N(OH) + H_2O$. The hydroxide produced is almost insoluble in water, explodes on being heated, and forms with most of the acids yellow to brown coloured salts, which are also almost insoluble. Of these, the *iodide* is the best known, as it is formed as a brown precipitate when ammonia is added to an alkaline solution of potassium mercuric iodide (p. 668). Even extremely small amounts of ammonia can in this way be detected by the yellow-brown coloration of the liquid, and this reaction, called by the name of its discoverer, the Nessler reaction, is used both for the detection and the approximate determination of very small amounts of ammonia, such as occur, for example, in the ordinary water supply. For quantitative purposes the coloration which is produced by the water to be investigated, is compared with a series of colours produced by known, gradated amounts of ammonia (in the form of very dilute solution of ammonium chloride) under the same conditions.

Of the two other types, the chlorine compounds are the best known; they are formed by precipitating solutions of mercuric chloride under different conditions with ammonia. If a solution of the mercury salt is added in the cold to excess of dilute ammonia, the compound HgH_2NCl is precipitated as a white substance which, on being heated, sublimes with decomposition without previous melting. The sublimate consists chiefly of calomel, while a mixture of nitrogen and ammonia escapes; the latter generally blackens the sublimate of calomel: $6HgH_2NCl = 6HgCl + 4NH_3 + N_2$. This compound was formerly used as a medicament and was called *infusible precipitate.*

If the ammonia is allowed to act on the mercuric chloride in hot solution in the presence of much ammonium chloride, a liquid is obtained which is clear when hot and which on cooling deposits small crystals of a white salt; this is the chloride of mercurdiammonium, and has, therefore, the formula $HgH_6N_2Cl_2$. This formula can be resolved into mercuric chloride plus ammonia, $HgCl_2 + 2NH_3$; the complex nature of the salt is, however, seen from the fact that it does not evolve any ammonia with a solution of caustic potash, and is only decomposed by this reagent on being strongly heated. Since on being heated the salt melts to a clear yellowish liquid, it was called *fusible precipitate* to distinguish it from mercurammonium chloride or infusible precipitate.

Besides the above compounds, there are others belonging to the ammonia series which, however, will not be mentioned here, as they have not been investigated in sufficient detail.

Other Complex Nitrogen Compounds.—Another complex mercury salt containing nitrogen which must be mentioned is potassium mercurinitrite, $K_2Hg(NO_2)_4$, which is obtained by dissolving mercuric oxide in a solution of potassium nitrite (whereby there is an evolution of heat), and destroying the basic reaction with acetic acid. From the solution a finely crystalline, bright yellow salt is obtained, which has the above composition, and is readily soluble in water. The solution is neutral, and can be boiled without decomposition; it does not exhibit, therefore, any of the hydrolysis of the normal mercuric salts.

Further, mercury enters extremely readily into organic compounds containing the imide group, NH. The substances produced do not exhibit the reactions of mercury, and therefore contain this element in a complex. Since they belong to organic chemistry, however, the statement that they are characteristic of mercury must suffice here.

Compounds, further, containing the amide group, NH_2, show these properties, but in a less degree than the imido-compounds.

To this class also belong the cyanogen compounds, concerning which the necessary information has already been given (p. 667).

Complex Sulphur Compounds.—The tendency of the two elements, sulphur and mercury, to combine, which is disclosed in the great stability of mercuric sulphide, asserts itself also in the formation of complex compounds on allowing the lower oxyacids of sulphur and mercury compounds to come together. Thus, mercuric oxide dissolves in the normal alkali salts of sulphurous acid and thiosulphuric acid, with great rise of temperature and production of an alkaline reaction; in these two salts, most of the other difficultly soluble salts of mercury are also readily soluble. The cause in both cases is to be found in the disappearance of dimercurion, owing to the formation of a complex compound.

By dissolving mercuric oxide in potassium sulphite and crystallising, there is obtained the salt $K_2Hg(SO_3)_2$, which is the potassium salt of mercurisulphosion, $Hg(SO_3)_2''$; potassium hydroxide is also formed at the same time, and remains in the mother liquor. The existence of this salt in the strongly alkaline liquid is sufficient to show that we are here dealing with a complex compound of mercury, as mercuric oxide would be precipitated from an ordinary salt. In acid solution, decomposition soon occurs, with separation of mercurous sulphate.

The composition of the solid salt which is obtained by the action of mercuric oxide on potassium thiosulphate is less simple. It has the composition $K_{10}Hg_3(S_2O_3)_8$, and it has not yet been determined whether this also expresses the composition of the anion in solution, or whether we are dealing with a double salt formed from a salt with a more simple anion and potassium thiosulphate, such as $3K_2Hg(S_2O_3)_2 \cdot 2K_2S_2O_3$.

This salt is also very stable in alkaline solution; in acid solution, t deposits mercuric sulphide—in the black form when the separation takes place quickly, and red when it occurs slowly. The cause of thi difference lies in already known principles.

Thermochemistry of Mercury.—On account of the man slightly dissociated compounds which mercury forms, the thermochemical relations of that metal exhibit a greater diversity than i found in the case of the other metals. The law of thermoneutrality for example, which refers strictly only to completely ionised salts entirely loses its validity here, and instead of the heat effect bein zero on mixing two neutral salts, there is a more or less considerabl evolution of heat when with the ions of mercury there come togethe such ions as unite with these to form undissociated compounds.

Thus the heats of neutralisation of mercuric oxide with th different acids are as follows:—

Nitric acid	27 *kj*
Hydrochloric acid	79 ,,
Hydrobromic acid	146 ,,
Hydrocyanic acid	130 ,,
Hydriodic acid	192 ,,

The first four numbers are comparable, as they refer to th dissolved substances; the last refers to the solid mercuric iodide an is therefore too large by the unknown heat of precipitation (the hea of solution with opposite sign). The differences of the numbers giv the heat which is evolved in the mutual displacement of the respectiv ions. The three halogen compounds also dissolve with slight evolution of heat in the corresponding halogen compounds of potassium.

The heats of formation of the solid mercury compounds are a follows: mercurous oxide, Hg_2O, 93 *kj*; chloride, Hg_2Cl_2, 262 *kj* bromide, Hg_2Br_2, 205 *kj*; iodide, Hg_2I_2, 119 *kj*; mercuric oxide HgO, 87 *kj*; chloride, $HgCl_2$, 223 *kj*; bromide, $HgBr_2$, 169 *kj*; iodide HgI_2, 102 *kj*; sulphide, HgS, 20 *kj*.

It is very remarkable that the heat of formation of mercuric oxid amounts to 87 *kj*, while that of the sulphide is only 20 *kj*, although the latter is incomparably more stable than the former.

CHAPTER XXXV

SILVER

General. — On account of its remarkable properties and of its occurrence in the metallic state, silver is one of the longest known metals. It is also a typical example of a "noble" metal, *i.e.* one which does not undergo oxidation in the air either in the cold or in the heat; under the most varied conditions, it completely retains its metallic haracter, even externally. This resistibility, together with its fine ustre, its plasticity and comparatively scarce occurrence, have assured or silver its use for costly articles and for coinage. On account of he property possessed by many silver compounds of undergoing hemical change when exposed to light, this metal has found a very xtensive technical application in photography. Further, the difficult olubility of many silver compounds, especially the halogen derivatives, as conditioned the use of silver as a reagent in the laboratory, and as made it indispensable for such purposes.

In its chemical behaviour, silver exhibits various relationships. A ond of union with the alkali metals is formed by its elementary ion; ome silver compounds are also isomorphous with the corresponding odium compounds. The difficult solubility of its halogen compounds llies it to the cuprous, mercurous, and the thallous compounds; the ast named metal forms the connecting link between silver and the lkali metals. Silver is a metal of a fine white colour, which melts at 45°, and in the air behaves indifferently towards the oxygen and ater vapour. It is attacked, however, by sulphuretted hydrogen, being onverted into silver sulphide; many organic sulphur compounds, and he soluble metallic sulphides, act similarly. Even at a comparatively gh temperature, oxygen under ordinary pressure does not act on lver; if, however, the pressure is increased, the pressure of decomposion of silver oxide is soon exceeded, and the latter is formed from ver and oxygen.

Besides the white silver in coherent condition, there are other rms of this metal. Thus, when silver is precipitated in the metallic ate from solutions by means of reducing agents, it can assume a great variety of colours according to circumstances. It appears that th yellow and brown forms of silver, more especially, which separate ou under the action of light on mixtures of silver salts and organi substances (which have a reducing action), are amorphous; they a more quickly attacked than the grey and black forms of silver, an also change into these under the influence of catalysers.

Metallic silver also has the property of passing into the colloid condition. This colloidal silver is obtained by reducing silver i alkaline liquids, and also when an electric arc is produced betwee silver electrodes under water; by the latter means, the silver is fir volatilised and then suddenly precipitated in the surrounding wate whereby it passes into the less stable form of colloidal silver. The solutions are of a brown or red colour; the forms of colloidal silv obtained by chemical means, dry up to masses with a metallic lustr the colour of which can be altered by slight influences, so that it pass through all shades of yellow, red, violet, and green. Notwithstandin their metallic lustre, these masses do not behave like metallic silve since they do not conduct the electric current. They are unstabl and are converted by many catalytic influences into ordinary white grey silver.

Silver is not attacked by dilute acids except nitric acid, whi readily dissolves it with evolution of nitric oxide and formation silver nitrate. It dissolves to the sulphate, also, in concentrated boi ing sulphuric acid, whereby sulphur dioxide escapes. It is ver resistant to basic substances; crucibles and dishes of silver are used the laboratory in working with caustic potash and soda, as that met is not attacked to any considerable extent even on fusing these su stances.

In the pure state, silver is a white, tenacious metal, which can readily drawn into wire and made into very thin sheets by rolling hammering. For use, it is alloyed with 10 per cent of copper in ord to make it harder. It conducts heat and electricity very well, ar occupies, in this respect, the first place among the metals.

The *combining weight* of silver is an important magnitude, since account of the excellent properties of its halogen compounds f analysis, many other combining weights have been determined means of these. The following method has been used in order establish the combining weight of silver with respect to oxygen.

Weighed quantities of silver chlorate were reduced to silv chloride; since three combining weights of oxygen are contained one combining weight of chlorate, we have the proportion :—

$$\frac{\text{loss of weight of chlorate}}{\text{weight of silver chloride}} = \frac{3 \times \text{combining weight of oxygen}}{\text{combining weight of silver chloride}}.$$

Thus, in one experiment, 103·980 gm. of silver chloride we obtained from 138·789 gm. of silver chlorate. Since the threefold combining weight of oxygen is, in accordance with our assumption (p. 143), 48·000, the combining weight of silver chloride is 143·381.

Silver was now converted into silver chloride. If the combining weight of silver chloride is divided in the same ratio as that in which analysis has shown these elements to be combined in silver chloride, the two separate combining weights are obtained.

Thus, 144·207 gm. of silver chloride were obtained from 108·579 gm. of silver. We have therefore the proportion :—

$$Cl : Ag = (144{\cdot}207 - 108{\cdot}579) : 108{\cdot}579,$$

where Cl denotes the combining weight of chlorine, and Ag that of silver. Hence :—

$$Ag = 107{\cdot}93 \text{ and } Cl = 35{\cdot}45.$$

Argention.—Silver forms only one kind of elementary ion, viz. monovalent argention, $Ag^{\cdot}$. Besides this, it can enter into many complex ions, especially such as contain nitrogen and sulphur.

Argention is colourless, and with respect to the properties of its compounds, it is allied to the monovalent ions of copper and mercury. On the other hand, there exist relations of isomorphism with sodium. It is the ion of a strong base, for the soluble silver salts react quite neutral and exhibit no hydrolysis, although almost all the salts of the heavy metals do.

This is not in conflict with the fact that argention passes readily nto the metal and is formed from this with difficulty, for we are dealing in the two cases with essentially different chemical relations and transformations. The heat of formation of argention from the metal has a large negative value ; – 106 *kj* must be absorbed in order that silver may pass into its ion. Metallic silver is also readily prepared from its salts ; as a rule, contact with any organic substance, especially in light, is sufficient for this, these substances then becoming brown or black in colour owing to the finely divided silver which separates out.

Argention is a strong poison for all organisms. Its actions, however, are restricted by the chloridion, which is everywhere present, and with which it forms a difficultly soluble compound.

Silver Oxide.—From the solutions of the silver salts, soluble bases do not precipitate the hydroxide as one would expect, but its nhydride, silver oxide, Ag_2O. This is a brown powder, which is ufficiently soluble in water to impart to it an alkaline reaction to egetable dyes, and which combines very readily with acids to form ilver salts. In the laboratory, it is used to remove halogen from dissolved halogen compounds, and to replace it by oxygen or hydroxyl. or this purpose, it is freshly prepared, or after being prepared, it is kept under water, since it coheres together on drying, and is then prevented by its physical condition from complete reaction.

On being heated, silver oxide decomposes even under a red-heat with evolution of oxygen, and a white powder of silver is left behind.

Silver Nitrate, $AgNO_3$, is the most important of the soluble silver salts. It is obtained by the dissolution of metallic silver in nitric acid. Since ordinary silver contains copper, the silver nitrate is freed from the copper salt which is formed at the same time by evaporation and fusion. The copper nitrate is thereby decomposed into copper oxide, which remains behind, and nitrogen peroxide and oxygen, which escape, while the silver nitrate is undecomposed. By treating the residue with water and filtering from the copper oxide, a pure solution of silver nitrate is obtained.

Silver nitrate is very readily soluble in water. It crystallises from solution in monoclinic, anhydrous crystals which, in the pure state, are colourless and stable, but in contact with organic substances, especially under the action of light, they are reduced and become blackened. For this reason, and on account of its action on the albuminoids, with which it forms insoluble compounds, it is used in medicine as a cauterising agent, and from this it has derived its trivial name *lunar caustic.* For this purpose, it is usually cast into thin rods; the melting point of the salt is very low, viz. 200°. Silver nitrate is also soluble in alcohol, especially if the latter contain water.

In the laboratory, the solution of silver nitrate is used for the detection and determination of the halogen ions, which combine with argention to form difficultly soluble compounds. It is also used as the starting substance in the preparation of the compounds used in photography.

Silver Chloride.—When argention and chloridion come together in aqueous solution, there at once separates out, if the solutions are not extremely dilute, a white precipitate which becomes flocculent on being shaken, and turns grey on being exposed to light. This is silver chloride, AgCl. The compound also occurs in nature, and, on account of its outward appearance, is called *horn-silver;* it is a brownish substance which can be cut with a knife.

Silver chloride is soluble to an extremely small degree in water measurements have shown that at medium temperatures 1·5 milligm of the substance is contained in one litre of saturated silver chloride solution. It is considerably more soluble in concentrated solutions o other chlorides; this is probably due to the formation of small quantitie of complex compounds, a well-marked type of which we shall later find in the case of silver cyanide. Silver chloride also dissolves in ammonia and in thiosulphates; the cause is, in this case also, the formation o well-known complex compounds.

When exposed to light, silver chloride passes into a grey-viole coloured substance, which is not metallic silver, as it does not dissolv in dilute nitric acid. It has recently been shown that silver sub-chloride, Ag_2Cl or Ag_4Cl_2, is here formed, which can be again converted into silver chloride by means of chlorine. Under the influence of the light, a decomposition of the silver chloride into sub-chloride and free chlorine occurs; equilibrium is established when the concentration of the chlorine in contact with these two substances has reached a definite value. This value is all the greater the stronger the light, and becomes vanishingly small in darkness. In the case of this equilibrium, therefore, the strength of the light plays a rôle similar to that of temperature in the decomposition of calcium carbonate by heat.

If the decomposition is carried out under such conditions that the chlorine can pass into other compounds, it is unlimited, and occurs in proportion to the strength of the light and to the time. The use of silver chloride for making copies of photographic negatives, depends on this. The binding of the liberated chlorine is effected by the organic compounds which are always present.

* The action of light on silver chloride takes place more slowly than in the case of the other halogen compounds of silver. It is therefore not used for taking photographs directly, as it is not sufficiently sensitive for this purpose.

* In the case of silver chloride, it is the blue and the violet rays that exhibit the greatest chemical activity. The region of active rays, however, can be shifted to a considerable extent by the presence of other substances.

Silver chloride is the form in which chloridion is identified and determined; the determination is effected by adding excess of silver nitrate to the solution in question, and filtering off and weighing the silver chloride produced.

Conversely, silver can be determined in the form of silver chloride. This method has been elaborated chiefly for the determination of this metal in bar-silver in governmental mints. The method is carried out by dissolving a weighed amount of the metal, and adding a solution of sodium chloride of known strength until a precipitate just ceases to be produced. The property of silver chloride of cohering together, renders this method possible; for a solution which still contains an excess of silver can be made quite clear by shaking, because the silver forms into flakes, which in a few moments sink down and leave a clear liquid. It is easy to see if a turbidity is produced in this on the addition of sodium chloride. This is historically the first case in which the method of volumetric analysis (p. 187) was elaborated.

Silver chloride accumulates from many chemical analyses; further, it is a form of compound into which other silver compounds can be readily converted, and in which it can be separated from other substances. The need often arises, therefore, of again preparing metallic silver, or other compounds of silver, from the silver chloride. This is most simply done by pouring dilute acid over the washed chloride and placing a rod of metallic zinc in the paste. There then occurs the reaction $2AgCl + Zn = ZnCl_2 + 2Ag$, and the chloride is reduced to grey silver powder. This is freed from zinc chloride by washing, and then readily dissolves in dilute nitric acid, forming silver nitrate.

Silver Bromide, $AgBr$, is similar to silver chloride, but is considerably less soluble than this. It is obtained as a yellowish-white, very fine precipitate from solutions in which its two ions come together. It changes colour in light similarly to silver chloride, and in accordance with the same laws. In ammonia, silver bromide is much less soluble than silver chloride, but it still dissolves fairly readily in thiosulphates.

Silver bromide is the most important substance for photographic pictures, since the photographic plates at present used are chiefly made with this. For their preparation, ammonium bromide is added to a solution of colourless glue or gelatine, and to this a solution of silver nitrate is added, light being excluded, and care also being taken that there is an excess of the bromine salt. Through the presence of the gelatine, the silver bromide is precipitated in a very fine, almost colloidal condition. The precipitate is warmed some time with the gelatine, whereby the silver bromide becomes larger grained, and also increases in sensitiveness, *i.e.* power of being affected by the light.[1] When the desired condition has been reached, the mass is cooled until it has become firm, and the ammonium nitrate which is formed and the excess of ammonium bromide are washed out with water. The washed mass is then drained, liquefied by warming, and used for coating glass plates; after drying, the glass plates are ready for exposure.

These "silver bromide-gelatine plates" can be made exceedingly sensitive to light, so that exposures in a camera of less than a thousandth of a second are sufficient to produce a picture.

At first, nothing can be seen on the exposed plate; it must be "developed." Developing consists in placing the plate in a reducing liquid. For this purpose there is used either a solution of potassium ferro-oxalate (p. 582), or alkaline solutions of various organic compounds. These liquids have the property of decomposing the silver bromide into bromidion and metallic silver; the latter separates out as a black powder. Owing to the exposure, now, the plate has acquired the property that the reduction takes place first, and most strongly, at those parts which have experienced the strongest illumination, and gradually more weakly where the illumination was weaker. A picture is therefore produced on the plate in which the bright parts contain a dense, the dark parts a slight or no precipitate. If, after sufficient development, the remaining silver bromide is removed by dissolving in sodium thiosulphate, a "negative" is obtained, *i.e.* a picture with opaque high-lights and transparent shadows.

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[1] This "maturing" of the silver bromide takes place much more quickly in ammoniacal than in neutral solution. On what this depends, has not yet been made clear; probably there is an incipient reduction to sub-bromide under the influence of the gelatine, and it is in accordance with known laws that reduction takes place more quickly in alkaline than in neutral or even acid solution.

On what the property of the illuminated silver bromide of being more quickly reduced depends, is still somewhat a matter of dispute. By far the most probable view is that under the action of the light an incipient reduction occurs, and therefore a picture of silver sub-bromide exists even in the undeveloped plate, and is invisible only on account of its small density. This is confirmed by the fact that by treatment with free bromine or any other oxidising agent, the "latent" picture is made to disappear, *i.e.* its power of being developed is destroyed.

The development, now, depends on the fact that a supersaturated solution of silver is produced by the reducing liquid, from which metal is deposited at those parts where there are already nuclei of silver present (p. 484). These are presumably formed by the developer from the readily reducible sub-bromide.

Silver Iodide, AgI, is also immediately formed when its ions come together, and of the three halogen compounds of silver it is by far the most difficultly soluble. It is a yellow powder which is dissolved only in traces, even in ammonia, and requires comparatively large amounts of sodium thiosulphate for its solution. It readily dissolves, however, in potassium cyanide. This proves that the concentration of argention is relatively greatest in its complex ammonia compound, is smaller in the thiosulphate compound, and is smallest in the cyanogen compound.

* Silver iodide was formerly chiefly used as photographic substance, and this both for the method of Daguerre (the first real photographic method) and for the later collodium process which is still in use for particular purposes.

* The method of Daguerre depends on the fact that the "development" of an exposed silver iodide plate is accomplished by exposing the illuminated plate to the vapours of mercury.[1] A plate of silver (or of copper coated with silver) is exposed to the vapours of iodine,

illuminated in the camera, and finally introduced into mercury vapour. The small drops of mercury are then precipitated chiefly on those parts which have been most illuminated, and when the plate is so viewed that the parts remaining bright reflect a dark surface, the dull parts coated with mercury appear bright, the other parts dark; a positive is therefore directly obtained.

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[1] The history of the discovery of this method is instructive; it is related as follows. Daguerre had first attempted to utilise directly the blackening of silver iodide in light, and had directed his efforts to preparing the layer in such a way that the blackening should occur as quickly as possible. On one occasion he had just begun to take a picture, but had to interrupt his work, and since no blackening had as yet made its appearance on the plate, he intended to use it for a further experiment, and placed it therefore in a dark press. Next day he found the picture on the plate. He was soon able to assure himself that a picture was always produced when he placed a plate, after a short exposure, in the press, but was unaware as to which of the objects present in the cupboard produced this effect. He therefore removed these objects one after the other, but still always obtained pictures even when the cupboard was quite empty. In other cupboards, under the same conditions, no picture was produced. Finally, he discovered some mercury which had been spilt in the joints of the wood, and on making the appropriate experiment, he found that the picture was developed by being left over metallic mercury.

That the mercury vapour is deposited differently on the illuminated parts from what it is on the non-illuminated, was subsequently recognised as a case of a general phenomenon; every change in a surface conditions a change in the condensation of a vapour, apparently owing to the alteration of the "metastable limit" (p. 117).

* In the collodium method an iodide is dissolved in collodium (a solution of gun-cotton in ether, which, on evaporation of the ether, leaves the dissolved substance behind in the form of a glassy skin), the collodium spread on a glass plate, and this then introduced into a solution of silver nitrate. Silver iodide, which is sensitive to light, is then precipitated in the layer. In this case also the picture must be developed. The development is carried out with a solution of ferrous sulphate, which reacts with the silver nitrate which moistens the film, and causes a separation of silver. This separation does not take place instantaneously, and the separated silver is deposited chiefly on the illuminated parts. The theory of this development is therefore the same as in the case of the silver bromide plates, and depends on the behaviour of nuclei towards supersaturated solutions. After development the plate is treated with a solution of potassium cyanide, in which the excess of silver iodide is dissolved, while the silver of which the picture consists remains undissolved.

* The silver iodide method has in most cases been superseded by the silver bromide method, because the silver bromide plates can be prepared any length of time before being used, and are also much more sensitive to light, whereas the silver iodide plates must be used wet. The latter, however, give sharper and clearer pictures, and are used in cases where this property is of especial importance, *e.g.* in the photomechanical preparation of printing blocks.

Silver Sulphate, Ag_2SO_4, is a rather slightly soluble salt which is obtained by the action of concentrated sulphuric acid on metallic silver. It is more soluble in dilute sulphuric acid, with formation of an acid salt. It is isomorphous with anhydrous sodium sulphate.

Silver Carbonate, Ag_2CO_3, is obtained as a bright yellow-coloured precipitate by the precipitation of a soluble silver salt with a soluble carbonate. The existence of the normal carbonate is a further proof that silver hydroxide is a strong base, since otherwise in the case of the heavy metals the partially hydrolysed basic carbonates are almost the only ones that can be obtained from aqueous solution.

Silver Sulphide, Ag_2S, is formed as a black-brown precipitate when silver solutions of any kind are treated with sulphuretted hydrogen. The sulphide is extremely difficultly soluble, and is also formed even in solutions in which silver is contained as a complex compound. The explanation of this is that the ions of the metals are also separated from the complex compounds, although generally in exceedingly small amount. In the case of the silver salts the concentration of the argention so produced is almost always sufficiently great for the small solubility product of the silver sulphide to be exceeded when sulphidion is added to the solution.

The ease with which silver sulphide is formed from metallic silver and sulphur compounds has been already mentioned (p. 673). It is made use of in analytical chemistry for the detection of sulphur in its compounds. The latter are fused with soda and charcoal, whereby sodium sulphide is formed, and the mass placed on moistened, polished silver-foil. If sulphur is present a brown stain is produced of silver sulphide.

Silver sulphide is readily oxidised by nitric acid and converted into silver sulphate. It undergoes the same transformation on being carefully heated in the air. A method of obtaining silver from the naturally occurring silver sulphide, silver glance, depends on this. The sulphate which is formed is extracted with hot water.

Silver Cyanide.—When argention and cyanidion come together, the compound AgCN separates out as a white precipitate, very similar to silver chloride, and is readily soluble in an excess of the cyanide, forming a complex compound which no longer exhibits most of the silver reactions. Only the precipitation with sulphuretted hydrogen occurs, in consequence of the very small solubility of silver sulphide.

The compound which is present in the solution is the salt of argenticyanidion, $Ag(CN)_2'$; on using potassium cyanide, therefore, potassium argenticyanide, $KAg(CN)_2$. From the solution the salt $KAg(CN)_2$ can easily be obtained in white crystals. Since the complex ion $Ag(CN)_2'$ is very stable, and splits off extremely little argention, the soluble cyanides are solvents for all silver salts except silver sulphide.

Potassium argenticyanide is used in the arts for the electrical deposition of silver on other metals. For the solutions of this salt have the valuable property that the silver is obtained from them in the form of a coherent coating, while in the electrolysis of the simple silver salts the metal is deposited crystalline. From the latter also silver is at once precipitated by chemical displacement on contact with the less noble metals which are to be silvered; it is then obtained in the form of a grey powder, and cannot adhere to the underlying metal, for the simple reason that the surface of this is dissolved in the chemical process.

In the solution of the complex salt, however, the concentration of the argention is so small that this direct reaction does not occur to a measurable extent, and the separation of silver takes place only on passing the electric current.

* On considering the formula of potassium argenticyanide, $K.Ag(CN)_2$, it is seen that the product of electrolysis should be, on the one hand, potassium, and, on the other, the discharged anion, $Ag(CN)_2$. Instead of this silver appears at the cathode, and the anode (consisting of silver) dissolves. We are dealing in both cases with so-called secondary reactions.

* The separation of potassion at the cathode would require a much higher potential than that of argention, in spite of the small concentration of the latter. Thus the conduction of the current in the electrolyte, it is true, is effected as far as the cathode by potassion. The transference of electricity at the cathode, however, occurs not by the discharge of potassion, but by that of the argention. Formally, the matter can also be expressed by saying that potassium is indeed formed, but at once undergoes double decomposition with the salt present with separation of silver, according to the equation $KAg(CN)_2 + K = Ag + 2KCN$. Silver and potassium cyanide are therefore formed.

* At the anode the ion $Ag(CN)_2'$ is discharged, and acts on the metallic silver, silver cyanide being formed according to the equation $Ag + Ag(CN)_2 = 2AgCN$. This is at once dissolved to potassium argenticyanide by the excess of potassium cyanide present, and the consumption of the latter is again made good by the potassium cyanide which is formed at the cathode. It is necessary, however, to keep the bath in movement, as otherwise the potassium cyanide would accumulate at the cathode, and would hinder the separation of the silver, while at the anode a deposition of silver cyanide would immediately occur on account of a lack of potassium cyanide.

Complex Salts in the Voltaic Cell.—When voltaic cells are constructed with silver in solutions of ordinary silver salts, it is found that silver is almost at the end of the potential series, which is a sign that the formation of the ion takes place with greater difficulty than in the case of most of the other metals, and conversely, the ion is very ready to pass into the metal. Thus with zinc there is obtained the potential 1·57 volt, and even with copper there is a potential of 0·47 volt (p. 635). If, however, the solution at the silver electrode is replaced by a solution of potassium cyanide, then according to the concentration of this the potential of silver sinks much below copper, and with very concentrated solutions can even sink below zinc. In the solution of potassium cyanide the silver loses its character as a noble metal, and acquires that of a readily oxidisable one. This is also apparent chemically, for if silver powder is shaken with a solution of potassium cyanide it is fairly rapidly dissolved, and on being acidified a white precipitate of silver cyanide is deposited from the liquid.

Similar phenomena are often found in the case of substances which form complex compounds with silver (and other metals behave quite similarly). To find the explanation we shall first make ourselves acquainted with another, generally smaller, deviation from the potential series.

Cells can be constructed in which one of the metals, instead of being surrounded by a *solution* of its salt, is in contact with its *solid* salt. This is the case, for example, in the lead accumulator, one electrode of which is formed of lead in solid lead sulphate (p. 653). If the potential of such cells is investigated, it is found that the particular metal has always shifted its position in the potential series, and always, without exception, *towards the zinc end.* Thus in a cell of zinc and silver there is found, when the zinc electrode is left unchanged :—

Zinc against silver in	silver nitrate . . .	1·57	volt
,, ,,	silver chloride . . .	1·06	,,
,, ,,	silver bromide . . .	0·93	,,
,, ,,	silver iodide . . .	0·66	,,

In the case of the iodide, therefore, the potential decreases by 0·91 volt, and is considerably different for the three "insoluble" salts.

The explanation is found on more closely studying the process which occurs on the passage of the current through such a cell. On the silver side the silver is transformed from the ionised state into the metallic. Argention, however, can exist only in *solution.* We must therefore conclude that, in spite of their apparent insolubility, all the above salts are really dissolved. This has also been proved in other ways, for if as pure water as possible is shaken with silver chloride the electrical conductivity perceptibly increases, *i.e.* conducting ions pass into the liquid, and these can only be silver and chloride ions, since none other are possible.

Now, the work which is necessary for the separation of an ion from its solution depends not only on the nature of the ion, but also on its concentration in the solution, and it becomes all the greater the smaller the concentration. Conversely, a metal passes all the more readily into its ion the smaller the concentration of this in the solution in which it is to be formed. If this is correct the position of every metal must be shifted towards the zinc end, when it is placed in a solution which is less concentrated in respect of its ion, and *vice versa.* It must therefore be possible to construct cells which will exhibit an electromotive force, simply by placing the same metal in two solutions of one of its salts of different concentration. This is indeed the case, and the currents which are thereby produced act always in such a sense that the metal in the dilute solution is dissolved; conversely, in the concentrated solution metal is deposited. In other words, the currents tend to equalise the differences of concentration.

The differences in the potential of the silver in the table given above are, therefore, the expression of the differences in the concentration of argention in the different cases, *i.e.* of the solubility of the respective silver compounds. Of the three halogen compounds the chloride is the most soluble, the iodide the least; this result agrees exceedingly well with other known facts.

On attempting to apply these considerations to the case of silver in a solution of potassium cyanide, there appears to be a contradiction, for silver occupies its remarkable position even in a solution of potassium argenticyanide, in which the amount of silver present can be very considerable. The contradiction is removed on reflecting that it is not a question of the absolute concentration of *silver* in the solution, but of the concentration of the *argention*. This and this alone is determinative for the electrochemical interchange between the electrode and the solution, and as we already know that the concentration of argention in the complex solutions is very small, the agreement is perfect.

This result can be still somewhat more closely tested. It has been stated that silver iodide readily dissolves in potassium cyanide. According to the doctrine of the solubility product, this is possible only if the concentration of argention in the solution of potassium cyanide is smaller than in the saturated aqueous solution of silver iodide. If, however, this is the case, then the potential of the silver in the solution of potassium cyanide must be shifted more towards the zinc end than in the solution of potassium iodide. This has been shown by experiment to be the case. In a moderately concentrated solution of potassium cyanide containing silver, the potential of silver against zinc was found to be 0·26 volt, while for silver iodide it is 0·66 volt.

Silver Thiocyanate.—Silver thiocyanate, $AgSCN$, is, in appearance and solubility, very similar to the chloride. It is formed as a white flocculent precipitate when its ions come together in aqueous solution.

On account of the ease with which thiocyananion can be detected by means of triferrion (p. 575), it is employed for the determination of silver in analysis. For this purpose a ferric salt (generally iron alum) is added to the silver solution, which is then acidified with nitric acid. Into this a solution of potassium thiocyanate of known strength is allowed to flow from a burette until the red colour of the ferric thiocyanate remains after stirring. The amount of silver present is proportional to the amount of thiocyanate solution employed.

In the same way, the halogen ions can be determined by adding to the solutions a known excess of silver solution, and titrating back the latter with thiocyanate solution. While this method possesses no difficulty in the case of bromidion and iodidion, the reaction is somewhat less definite in the case of chloridion, because when the titration is finished the slight excess of thiocyananion present undergoes double decomposition with the silver chloride, and the iron coloration thus becomes much weaker. This difficulty can be avoided by first filtering off the silver chloride; the method, however, thereby loses much of its simplicity.

Complex Silver Compounds.—In the preceding descriptions of the silver compounds mention has repeatedly had to be made of the complex compounds which are formed by silver. As in the case of mercury, these are chiefly nitrogen and sulphur compounds. The halogens, however, have much less tendency to form complex compounds with silver. For in the case of the latter the signs of the formation of such complexes are limited to the fact that the difficultly soluble halogen compounds of silver dissolve in the concentrated solutions of the corresponding alkali salts more readily than in pure water, and also that these solutions are not precipitated by caustic potash. Well-defined compounds are scarcely known in the solid state.

Of the complex compounds containing nitrogen the cyanogen compounds have been already treated (p. 681). The ammonia compounds are still deserving of mention. If ammonia is added to a silver solution, a precipitate of silver oxide is first formed. This, however, readily dissolves in excess of ammonia, and there is contained in the solution the complex ion $Ag(NH_3)_2^{\cdot}$. The corresponding salts are obtained in the solid state by evaporating the solution; the fine crystalline nitrate $Ag(NH_3)_2NO_3$ is particularly well known. By reason of the formation of this complex ion many difficultly soluble silver salts dissolve in ammonia solution. Since, however, the complex is partially, although very slightly, dissociated into argention plus ammonia, the solvent power is not unlimited. The saturated solution of silver bromide has approximately a concentration corresponding to the concentration of argention in the solutions of the silver ammonia salts. Equilibria can therefore be observed when ammonia acts on silver bromide, for the solubility is found to be limited, and is greatly restricted by the presence of the other ion, bromidion. Finally, the solubility of silver iodide is so much below the concentration of the argention in the ammoniacal solution that it is scarcely dissolved to an appreciable extent.

Besides the above complex, others apparently exist in which the components are in other proportions, but as yet nothing definite is known of these. In any case the one mentioned is the most stable.

Silver also readily replaces the hydrogen of the imido-group, NH, with formation of corresponding complexes. These, however, chiefly belong to organic chemistry, and cannot be discussed here. The hydrogen of the amido-group, NH_2, is also replaced by silver.

The solubility of silver compounds in *thiosulphates* is also due to the formation of complexes. These can be regarded as thiosulphates in which hydrogen is replaced by silver—in such a way, however, that the saline compound which is formed does not dissociate like an ordinary salt into ions, but remains combined. In this way only *one* of the two combining weights of the hydrogen of the thiosulphuric acid is replaced. Since it is assumed that one of these is present in the thiosulphuric acid as hydroxyl, the other as sulphhydryl, the further assumption is probable that the silver replaces the hydrogen of the sulphhydryl, because its power of combining with sulphur is certainly more highly developed than its power of combining with oxygen. The argentithiosulphanion which is here formed would therefore have the formula $AgS.SO_3'$.

From the solutions obtained by the saturation of sodium thiosulphate with silver salts two different salts crystallise out. One of these is difficultly soluble, and its composition corresponds to the above formula, the hydrogen being replaced by sodium; the other is readily soluble, contains twice as much sodium, but its nature has not yet been cleared up. The formulæ of these salts are $Na(SO_3.SAg)$ and $2Na(SO_3SAg) + Na_2S_2O_3$.

The complex character of the compounds is proved not only by the solubility relations, but also by the fact that they both have a remarkably sweet taste, whereas otherwise the silver compounds have an unpleasant, metallic, astringent taste.

The formation of these compounds occurs when sodium thiosulphate is employed to dissolve difficultly soluble silver salts. This application is very widely extended in photography. If it is desired to separate the silver from them, an alkali sulphide, which precipitates silver sulphide from the solution, is the most suitable for the purpose. The solubility of silver sulphide is so small that it is practically completely precipitated even from the complex compound.

Sodium sulphite behaves similarly to sodium thiosulphate. A salt, $Na(SO_3)Ag$, which is difficultly soluble in water, and which can be regarded as the sodium salt of argentisulphurous acid, is also known.

Metallurgy of Silver.—Most of the silver is obtained as an admixture in lead in the preparation of the latter metal from galena (p. 655). For the purpose of separating the two metals use is made of the difference of their behaviour to oxygen. The lead containing silver is fused and exposed to the action of the atmospheric oxygen; the lead is thereby oxidised, its oxide flowing off as litharge, and the silver remains behind. The completion of the separation is recognised by the disappearance of the coating of lead oxide and the appearance of the lustrous surface of the silver (the "fulguration of silver").

If the argentiferous lead, or "work-lead," is very poor in silver, it is more advantageous to separate it by means of a process of crystallisation into pure lead and an alloy richer in silver. This is done by allowing the fused work-lead to slowly cool. Pure lead then crystallises out and a mother liquor, comparatively rich in silver, remains behind, just as from a salt solution pure water crystallises out as ice and a mother liquor richer in salt is formed. By continuing this separation, a condition is finally reached in which silver also begins to separate out, *i.e.* in which the solution is saturated in respect of silver. A further separation in this way is then impossible, since the mixture of lead and silver which separates out has the same composition as the mother liquor.

For the above purpose, use is also made of the law of distribution (p. 230), the work-lead being fused with zinc. In the liquid state these two metals are almost immiscible; the silver is, however, much more soluble in zinc than in lead. The work-lead, therefore, behaves towards zinc like an aqueous solution of iodine towards carbon disulphide (p. 230), and the silver passes for the most part into the zinc. The layer of zinc rich in silver is allowed to solidify and removed from the desilverised lead. The two metals can be separated by heating in a current of steam, whereby the zinc is oxidised, or by treating with dilute acids, whereby it is dissolved.

Besides this method there are also many others. Certain ores of silver are roasted with addition of common salt; the silver thereby passes into silver chloride, which can be extracted with a concentrated solution of sodium chloride, ammonia, potassium cyanide, or sodium thiosulphate. In other cases when silver sulphide is present, the latter can be converted by roasting into silver sulphate, which is extracted with hot water and converted into silver by means of copper or iron. Various methods depend on the use of mercury for the reduction and extraction of the silver; finally, silver which has in any way been converted into aqueous solution, can be readily precipitated in the metallic state by the electric current.

Eutectic Mixtures.—The phenomenon which has just been mentioned, that from a liquid mixture, a mixture of solid substances separates out having the same composition as the solution, is not limited to the present case, but is of universal occurrence, being met with in all cases where two substances A and B can be mixed in the liquid state in all proportions.

To get a clear idea of this, we represent the composition of the liquid mixtures along the line *AB* (Fig. 118) by dividing this in the ratio of the amounts of substance present in the solution; *A* therefore represents the pure substance A, *B* the pure substance B, and every point lying between these, a mixture of the two.

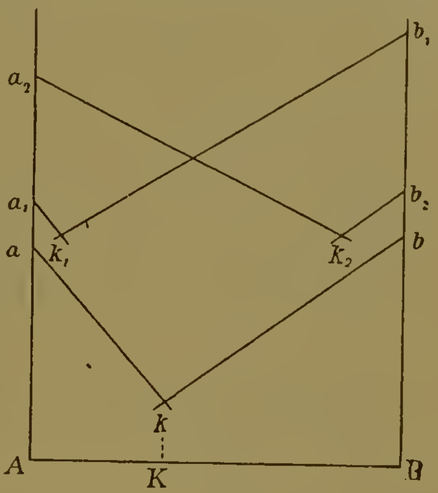

FIG. 118.

The temperatures at which the corresponding mixture is in equilibrium with solid substance are measured perpendicular to *AB*. The melting point of *A* is then represented by *a*, and that of *B* by *b*.

If a small quantity of *B* is added to pure *A*, the melting point of the latter falls, in accordance with the general rule (p. 155), the depression being all the greater the larger the amount of *B* added. The change is almost proportional to the amount added, so that the corresponding temperatures are represented by an almost straight line *ak*.

The same considerations can be applied to *B*; from the point *b* a straight line must also sink towards the left representing the temperatures at which the liquid mixture is in equilibrium with solid B, *i.e.* the melting points of *B* in presence of the mixed liquid. The two lines will cut in a point *k*.

Now, along *ak* the liquid is in equilibrium with solid A, along *bk*, with solid B. In the point *k*, therefore, the liquid is in equilibrium with both solid substances, and as the two lines cut only in one point, there is only *one* liquid mixture which is in equilibrium at one and the same time with the two solid substances.

This follows also from the phase law. We have two components, and in the point *k* four phases are present, viz. the liquid, the two solid substances, and vapour.[1] There is therefore no degree of freedom remaining, and all the variables, viz., pressure, temperature, and composition, have definite values.

If, therefore, any liquid mixture whatever is cooled, that one of the two substances will separate out which is in excess with respect of the composition represented by the point *k*. This continues with fall of temperature until the point *k* is reached. At this point the two substances separate out at the same time and in such proportions that the melting point and the composition of the liquid remain unchanged. A mixture corresponding to *k* behaves, therefore, like a simple substance, for it exhibits a constant melting point although it is a mixture. The relations are very similar to those in the case of acids of constant boiling point (p. 182).

Such a mixture of constant melting point is called a *eutectic mixture*, and the point *k* the *eutectic point*. The melting point of a eutectic mixture is, necessarily, always *under* that of its components, and is all the more so the nearer the melting points of the two pure substances are to one another. Fig. 118, in which various possible cases are represented, allows of these relations being readily seen.

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[1] If the vapour is excluded one degree of freedom is obtained, *i.e.* the point *k* moves (very slightly) with the pressure.

CHAPTER XXXVI

THALLIUM

General.—Thallium occupies a remarkable intermediate position between various other elements. By reason of the physical properties of the free element, it is allied to lead, for, like this, it is soft, ductile, and has a high density. Its hydroxide, which is readily soluble in water, procures it a position along with the alkali metals, with which it is isomorphous in various compounds; its difficultly soluble halogen compounds bring it near to silver, copper, and mercury, and in another series of compounds it exhibits relations to the trivalent elements aluminium and iron.

Thallium was discovered by means of the spectroscope; all its compounds on being heated in the Bunsen flame, in which they quickly volatilise, give a green coloration which on being examined with the spectroscope appears as a single bright green line.

Thallium occurs only in small quantity in nature, but like all the elements which can be detected in small amounts, it has been found to be fairly widely distributed. It is obtained as a by-product from the flue-dust in sulphuric acid works in which pyrites containing thallium is employed, and also, in association with zinc, from zinc ores. In the latter way it could be obtained in fairly large amounts if there were any demand for it.

As has already been mentioned, metallic thallium is very similar to lead, but is still softer. Its density is 11·9, its melting point 290°. It makes a grey mark on paper, but this soon disappears owing to oxidation. Fresh surfaces of the metal, which have an almost silver white appearance, quickly tarnish in the air through oxidation. In the potential series, it stands between cadmium and iron, and is therefore a metal which readily replaces hydrogen from dilute acids. As a matter of fact, it dissolves in dilute acids which do not form difficultly soluble salts, *e.g.* sulphuric acid and nitric acid, and is precipitated in he metallic state from its solutions by zinc and cadmium.

Thallium forms two kinds of elementary ions, monovalent monohallion, $Tl^{\cdot}$, and trivalent trithallion, $Tl^{\cdot\cdot\cdot}$. The former conditions the similarity of thallium to the alkali metals, the latter that to aluminium.

Thallous salts are formed with evolution of hydrogen by dissolving the metal in dilute acids. Solution in nitric acid, which takes place with reduction of the latter (very dilute acid yields hydrogen), also leads only to thallous nitrate. By means of free chlorine, however, thallous compounds can be converted into thallic compounds.

Monothallion is colourless; has, like lead, a poisonous action; and can be recognised by the formation of various difficultly soluble salts, especially the yellow iodide. It is not precipitated by alkali hydroxides and carbonates, and is thereby distinguished from the ions of all other heavy metals.

Thallous Hydroxide, TlOH, is obtained by the decomposition of thallous sulphate with baryta, as a liquid with a strongly alkaline reaction which is dissociated into its ions, monothallion and hydroxidion, quite as extensively as the alkali hydroxides, and exhibits, therefore, the same basic properties. It turns red litmus paper blue, renders turmeric brown, and makes the skin of the fingers slippery when moistened with it. On evaporating the solution, the yellowish coloured hydroxide crystallising with $1H_2O$ is obtained; in contrast with the hydroxides of the alkali metals, this very readily loses the elements of water and passes into thallous oxide or Tl_2O, which is black-brown in colour. The dehydration takes place even at the temperature of the boiling water, so that on evaporating a solution of the hydroxide on the water-bath, black-brown lines are formed at the edges, but these immediately disappear when the liquid is passed over them.

Thallous Sulphate, Tl_2SO_4, crystallises anhydrous in the rhombic forms of potassium sulphate, with which it is isomorphous. It is fairly soluble in water. With the sulphates of the trivalent metals, also, it forms double salts which crystallise in regular forms, and are perfectly analogous to the alums of the alkali metals. It can also form the corresponding monoclinic double salts with the divalent sulphates of the vitriol series.

Thallous Nitrate, $TlNO_3$, also crystallises anhydrous; it is soluble in about ten times its weight of water at room temperature, and melts at 205°. By mixing it with other nitrates, masses can be obtained which melt at a comparatively low temperature; these find application as heavy liquids (solid thallous nitrate has the density 5·8).

Thallium Carbonate, Tl_2CO_3, is an anhydrous salt which dissolves in twenty times its weight of water, yielding a liquid with an alkaline reaction. The salt dissolves more readily in water containing excess of carbonic acid, but the acid carbonate is not known with certainty in the solid state.

The *phosphates* and *borates* of monothallion are also soluble in water, so that in this respect also thallium is allied to the alkali metals.

Thallous Sulphide, Tl_2S, is a brown-black precipitate which is formed by sulphuretted hydrogen in neutral, but not in acid solutions of thallous salts. The solubility and therefore also the conditions of precipitation, are most nearly akin to those of zinc sulphide, although thallous sulphide appears to be somewhat more soluble. Accordingly, the precipitated sulphide redissolves in dilute acids.

Thallous Chloride.—In its halogen compounds, thallium is most closely allied to silver, for these substances are white or yellow difficultly soluble powders which are sensitive to light; their solubility also diminishes with increasing combining weight of the halogen.

Thallous chloride, TlCl, is obtained as a white precipitate which slowly darkens in the light, when the ions of the salt come together in solution. About three hundred times its weight of water is required to dissolve it.

It is insoluble in ammonia, but dissolves in sodium thiosulphate with formation of a complex compound. It exhibits no tendency to form complex compounds with soluble chlorides; the salt is therefore precipitated from aqueous solutions on the addition of hydrochloric acid or chlorides, owing to the increase of chloridion. It is converted into soluble thallic chloride by treatment with chlorine under water.

Thallous Bromide is a yellow-white precipitate, the solubility of which is considerably less than that of the chloride, to which, however, in its other properties, it is similar.

Thallous Iodide is deposited as a yellow precipitate even from very dilute solutions, when its ions come together. It requires 15,000 parts of water for its solution, and, for known reasons, it is still less soluble in a solution of potassium iodide. This salt is employed for the detection and separation of thallium. In dilute acids it is not appreciably more soluble than in pure water, as it is the salt of the strong hydriodic acid (p. 443).

Thallous Fluoride is, in contrast with the other halogen compounds, a readily soluble salt.

The trivalent *trithallion* is of a somewhat yellowish colour, and is formed from monothallion only by fairly strong oxidising agents, such as chlorine or permanganate. Conversely, it very readily passes again into monothallion.

Thallic Hydroxide is obtained as a brown precipitate similar in appearance to ferric oxide, on adding soluble bases to a thallic salt. On being dried it assumes the composition TlO(OH); the freshly precipitated substance is probably $Tl(OH)_3$. On being heated, the hydroxide loses water and readily also oxygen, so that it passes into thallous oxide. Thallic oxide, Tl_2O_3, is also obtained when solutions of thallous salts are subjected to electrolysis; it separates out at the anode as a black coating, but it is difficult to obtain it of a definite composition.

Thallic hydroxide is a very weak base; its salts are greatly hydrolysed in aqueous solution, and when the dilution is fairly great almost all the hydroxide is precipitated from it, the acid remaining in solution. The most stable is the chloride, which can be obtained from the sub-chloride by means of chlorine. The bromide is less stable, and on attempting to prepare the iodide a mixture of thallous iodide and free iodine is obtained.

Thallic Sulphate, $Tl_2(SO_4)_3$, can form alums with the alkali sulphates. The double salt from thallous sulphate and thallic sulphate, which should also yield an alum, has, however, another form and a different amount of water of crystallisation; its composition is $Tl . Tl(SO_4)_2 . 6H_2O$, in which the one Tl is monovalent and the other trivalent.

The combining weight of thallium is Tl = 204·1.

CHAPTER XXXVII

BISMUTH

General.—For the purposes of analysis, bismuth is classed along with the metals of the copper group, because it forms a sulphide which is insoluble in dilute acids as well as in alkali sulphides. According to its chemical affinity, however, it is so closely connected with antimony and arsenic, which belong to the last group, that it must be treated along with these, and is therefore suitably placed at the point of transition from the one group to the other. Of these elements it has the highest combining weight; for this reason, in accordance with the general rule, the basic properties are more strongly marked in it than in the case of its congeners. As the combining weight decreases, the latter rapidly lose their metallic character and the power of forming basic oxides, and finally lead to the non-metallic elements phosphorus and nitrogen, in which the acid forming properties are completely developed.

Metallic bismuth is a white, somewhat reddish metal of a well-marked crystalline character; it is brittle, is not ductile, and falls to a powder when struck with a hammer. It melts as low as 270°, and at a bright white heat passes into a vapour, the density of which leads to the molar weight 209, which coincides with the combining weight. It remains unchanged in the air, and is also very resistant to water. It is not attacked by dilute acids; its position in the potential series is between copper and silver, and it therefore inclines towards the noble metals. It therefore occurs in nature in many cases even in the uncombined state; it also occurs combined with sulphur as bismuth glance. Bismuth is readily dissolved by nitric acid with formation of bismuth nitrate and nitrous oxide.

Bismuth readily forms alloys with other metals whereby, in accordance with the general law, the melting point sinks. By the addition of lead, tin, and cadmium, alloys are obtained which liquefy even under 100°; they fuse therefore in boiling water.

The combining weight of bismuth has been determined by weighing the metal and the oxide obtained from it. It is not known with perfect certainty, and we shall take it as Bi = 208·5.

Bismuthion.—Bismuth forms one kind of elementary ion, viz. the trivalent bismuthion, $Bi^{\cdot\cdot\cdot}$. This is almost the only ion derived from bismuth, for the tendency of this metal to form complexes is extremely slight, and with the exception of some organic ions containing bismuth, others are scarcely known.

Bismuthion is colourless and forms an extremely weak base with hydroxyl. As a consequence, the phenomenon of hydrolysis is so marked in the case of the bismuth salts that it can be regarded as a characteristic in analysis. Since the basic compounds which are hereby formed are difficultly soluble in water, the bismuth salts are precipitated by mere dilution with water; the precipitate is again dissolved on the addition of acids.

The best known bismuth salt is the *nitrate*, which is obtained in hydrated crystals, $Bi(NO_3)_3 . 5H_2O$, by crystallisation from the solution of bismuth in nitric acid. On pouring water over these crystals, a snow-white, crystalline powder of a basic nitrate, $Bi(OH)_2NO_3$, is deposited, which is applied in medicine under the name of bismuth subnitrate. The nitric acid which is split off passes into the solution and enables another portion of the bismuth salt to remain dissolved. There exists, therefore, in the solution in respect of the precipitate of the basic salt, an equilibrium which is characterised by the fact that the concentration of the hydroxyl from the water is rendered sufficiently small by means of the hydrion of the free acid to allow the solubility product of the basic salt to be reached.

From solutions, bismuth hydroxide, $Bi(OH)_3$, is precipitated by excess of soluble bases. It is a white precipitate which is soluble neither in ammonia nor in caustic potash. The former behaviour is due to the extremely slight development of its basic properties; the latter shows that it cannot, as many other weak bases do, split off hydrion and yield an anion containing oxygen.

On being heated, the hydroxide loses water and is converted into bismuth oxide, Bi_2O_3, a yellow powder which, at a higher temperature, becomes reddish brown, melts, and becomes crystalline on cooling.

Bismuth sulphate, $Bi_2(SO_4)_3$, is obtained in the impure state by heating bismuth with concentrated sulphuric acid; treatment with water converts it into the difficultly soluble basic sulphate $Bi_2(OH)_4(SO_4)$. With potassium sulphate it forms a well characterised double salt, $KBi(SO_4)_2$.

When sodium thiosulphate is added to bismuth salts, a clear liquid is formed from which, owing to decomposition, bismuth sulphide is slowly deposited. The solution probably contains the sodium salt of a bismuth thiosulphuric acid, for on the addition of potassium salts and alcohol a difficultly soluble precipitate of $K_3Bi(S_2O_3)_3 + H_2O$ is deposited, which can be regarded as the potassium salt of the above acid. More exact investigations are still wanting as to whether (as is probably the case) a complex ion containing bismuth is here present. It has been proposed to employ the precipitate, which is of a yellow colour, for the detection and separation of potassium.

Bismuth Chloride, $BiCl_3$, is very readily formed from bismuth and free chlorine, the combination taking place with considerable evolution of heat. It is a white, soft, but crystalline substance which becomes very dark in colour through excess of bismuth; this points to the formation of a lower chlorine compound, perhaps BiCl, although no such substance has been prepared in the pure state. With water, the chloride at once deposits a snow-white precipitate of basic chloride, or rather, the anhydride of this, bismuth oxychloride, BiOCl. This substance has a certain similarity to the monovalent chlorides of silver and mercury, not only as regards its external appearance and its difficult solubility, but also in its property of becoming grey in light. Prominence can be given graphically to this similarity by assuming in this and in the similar compounds of bismuth, the monovalent ion $BiO^{\cdot}$, which has been called bismuthyl. This is, however, so far, only a formal assumption, since there is as yet no proof of the existence of such an ion in the solution.

Bismuth oxychloride, BiOCl, is so difficultly soluble in water that it can be employed for the precipitation of bismuth. For that purpose it is only necessary to introduce chloridion in some form into the solution and then to dilute this. The dilution must be so much the greater the more highly acid the liquid was at the commencement; it is advisable, therefore, when employing this method, to remove the excess of acid by means of a base.

The bromide of bismuth is very similar to the chloride, and forms also a very difficultly soluble oxybromide of a white colour.

Bismuth iodide is obtained from the elements or by the precipitation of bismuth salts with a large excess of potassium iodide, and is a black-red crystalline substance which is decomposed by water much more slowly than the other halogen compounds. With much water, bismuth oxyiodide is formed as a fine red powder.

Bismuth iodide dissolves in hydriodic acid and forms hydriodobismuthic acid, $HBiI_4 . 4H_2O$. With the iodides of the alkali metals, the salts of this acid are obtained; of these the potassium salt, $KBiI_4$, is known in the form of ruby-red laminæ. The complex anion of hydriodobismuthic acid, BiI_4', is, however, only slightly stable, and with much water decomposes into bismuth oxyiodide and free hydriodic acid.

Bismuth Sulphide, Bi_2S_3, is obtained as a black-brown precipitate on passing sulphuretted hydrogen into bismuth solutions. It is obtained crystalline by fusing metallic bismuth with sulphur; the bismuth sulphide which is formed dissolves in the metal and, on cooling, separates out in clusters. It occurs in nature as bismuth glance, and is used for the preparation of bismuth, which is obtained from the glance by roasting and reduction of the oxide formed with charcoal.

Bismuth sulphide is insoluble in dilute acids, but dissolves with evolution of sulphuretted hydrogen on being heated with concentrated hydrochloric acid. It is not appreciably soluble in alkali sulphides, a behaviour which is opposed to that of the sulphur compounds of its nearest congeners, antimony and arsenic. By fusing together bismuth sulphide and alkali sulphides, however, fine crystalline compounds, $KBiS_2$ and $NaBiS_2$, having a metallic lustre, can be obtained; these, however, rapidly oxidise in the air.

Other Compounds.—It was mentioned above that a lower chloride of bismuth probably exists, although it is not known as a pure substance. The existence of a corresponding oxygen compound Bi_2O_2, has also been asserted. It is obtained as a dark brown powder by the careful treatment of bismuth hydroxide with reducing substances.

A higher oxide of bismuth, *bismuth pentoxide*, Bi_2O_5, is obtained by treating the hydroxide with strong oxidising agents. Further, a mixture of bismuth oxide and caustic potash or soda when fused in the air is oxidised to a brown mass which, on being treated with water, deposits bismuth pentoxide contaminated with alkali. In the brown melt there possibly exists the alkali salt of a bismuthic acid; in aqueous solution, however, such salts cannot be obtained, as they are immediately hydrolysed. Bismuth pentoxide is obtained as a heavy, brown powder or as a hydrate of a red colour; it is insoluble in acids and bases, and is converted by hydrochloric acid into the trichloride, with evolution of chlorine.

CHAPTER XXXVIII

ANTIMONY

General.—With antimony we commence the consideration of the metals of the tin group, in which a number of elements are classed together belonging to different natural families and forming corresponding sub-groups. Their common characteristic is the predominating tendency to form acid compounds in place of the basic ones yielded by the other metals. Their oxides, especially those comparatively rich in oxygen, behave as the anhydrides of acids, and their sulphur compounds dissolve in the solutions of the alkali sulphides with formation of thio-salts (*vide infra*). The last characteristic which is of importance in analytical chemistry has given rise to the formation of the whole group, and the relations which are here met with will be presently discussed in greater detail.

On account of the manifold and widely extending affinity relations existing between the elements, we shall repeatedly find resemblances to other groups, and it would be possible to class several of the elements considered here along with others previously discussed. By reason, however, of the variety of the relationships, a system of the elements, sufficient in all respects, cannot be framed, and the arrangement which has here been retained has therefore been determined chiefly by didactic considerations.

Antimony.—Antimony is allied on the one hand to bismuth, and on the other, to arsenic and phosphorus. It therefore forms a transition element between the metals and the non-metals, but is still essentially on the side of the metals.

Antimony is a grey-white, lustrous metal, having the density 6·7; from the fused mass it solidifies in a distinctly crystalline form, and is at all temperatures so brittle that it can be easily ground or pounded to a powder. It melts at 440°, and volatilises at a high temperature. The vapour exhibits a variable molar weight in the neighbourhood of 290. This number corresponds to no simple formula, but lies between Sb_2 and Sb_3; probably, therefore, we are dealing with a mixture of different kinds of vapour, perhaps Sb_4 and Sb.

In the potential series, antimony stands beside bismuth; it does not, therefore, decompose dilute acids, and it also remains unchanged in the air. On being heated it readily oxidises; a piece of antimony fused on charcoal before the blowpipe, continues to glow even after the flame has been removed, the antimony burning to antimony oxide. If a small globe of strongly heated antimony is thrown on a piece of paper with upturned edges, it skips about on this, burning all the while, and leaves very regularly marked, hyperbolic trails (Fig. 119).

Besides the ordinary antimony, another form of less stability is known, which is obtained as a silver-white metal, of density 5·78, by slowly decomposing a concentrated solution of antimony chloride in hydrochloric acid with the electric current. The metal which is deposited falls to a powder with slight explosion on being scratched by a sharp body, ordinary grey antimony being formed with considerable evolution of heat. This allotropic metal is not pure but contains antimony chloride, the amount of which varies with the conditions of the experiment.

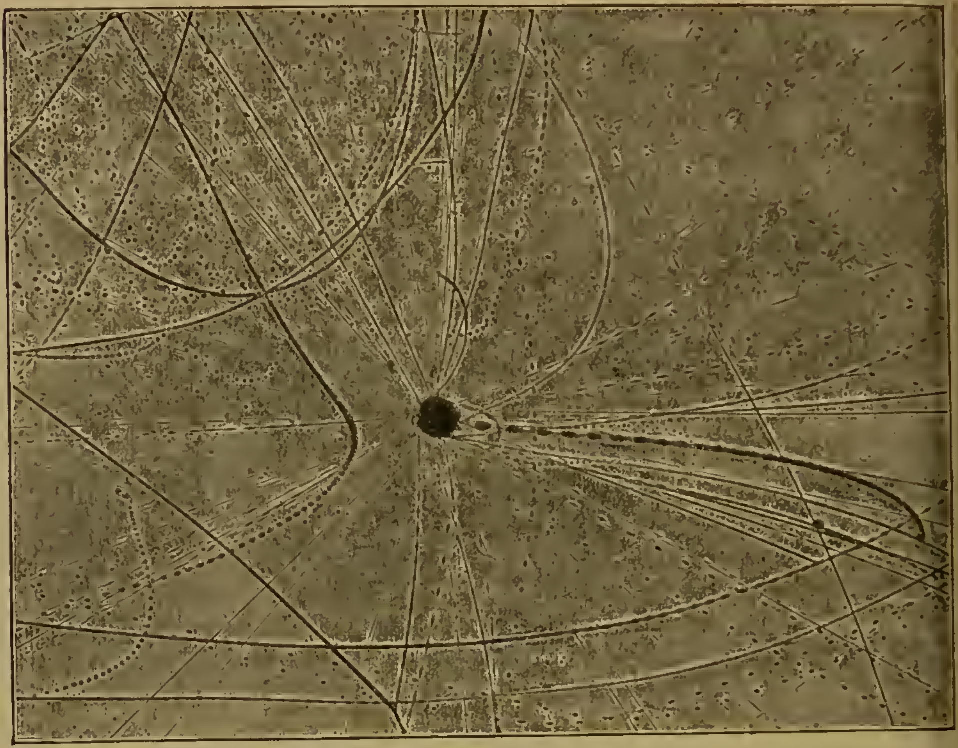

FIG. 119.

Ions of Antimony.—Antimony can form compounds of the trivalent and of the pentavalent type; only the former of these, however, yields a basic hydroxide, while the hydroxide of the latter type is an oxyacid. They each show the basic and acid character respectively only in a slight degree, and the number of well characterised salts of antimony is therefore not large.

The compounds of the trivalent type are the better known and the more stable; they are the only ones occurring in nature. The compounds of the pentavalent type are produced from the former by the action of strong oxidising agents, and can be readily reduced again.

The existence of a trivalent antimonion is probable, since there are solutions of antimony salts which behave in general like salts. These salts, derived from the base antimony hydroxide, $Sb(OH)_3$, are, however, greatly hydrolysed in water, and clear solutions can be obtained only with a large excess of acid. Consequently, the properties of the trivalent antimonion are not known with great exactness, and it can only be said with regard to it, that it is colourless and has a very poisonous action on the organism of the higher animals. In small quantities it acts as an emetic.

Antimony Hydroxide, $Sb(OH)_3$, is obtained as a white precipitate by the hydrolysis of the salts of antimony; it readily loses water and is converted into the anhydride, antimony oxide Sb_2O_3. It can be converted into salts by treatment with concentrated acids; these again undergo decomposition on dilution with water. It dissolves in caustic alkalis; it has therefore the power of splitting off hydrion and of acting as an acid, in a similar manner to alumina. The corresponding salts are reducing agents, and, for example, precipitate silver in the metallic state from its salts.

Antimony oxide, Sb_2O_3, crystallises readily and proves to be dimorphous, crystallising either in regular or in rhombic form. The first form has the density 5·3, the second, 5·6. It has not yet been established which of the two forms is the more stable; it appears, however, to be the rhombic, since this occurs much more abundantly in nature. They are both, at all events, more stable than the hydroxide, since the latter, even under water, passes into the crystalline oxide.

Antimonious Chloride, or antimony trichloride, $SbCl_3$, is obtained from metallic antimony and chlorine by using excess of the former; it is obtained more cheaply by heating antimony sulphide with concentrated hydrochloric acid, whereby sulphuretted hydrogen escapes. The aqueous solution is evaporated and distilled, whereupon anhydrous antimony trichloride passes over. The remarkable fact that the chloride does not hereby decompose into hydrochloric acid and antimony oxide, as *e.g.* aluminium chloride does, although alumina is a stronger base, is probably due to the fact that in concentrated solution antimony trichloride is very slightly dissociated into its ions, and therefore undergoes hydrolysis in a correspondingly slight degree.

Antimony trichloride is obtained as a white, crystalline, semi-solid mass (butter of antimony), which melts readily and boils at 220°. It is decomposed by water, difficultly soluble oxychlorides being deposited; the composition of these depends on the amount of water, the amount of chlorine which they contain being all the less the larger the quantity of water.

Of these, the compound $Sb_4O_5Cl_2$, being a crystalline substance, is best characterised, but even it decomposes into antimony oxide and hydrochloric acid on being treated with more water.

Antimony trichloride combines with hydrochloric acid to form a complex hydrochloroantimonic acid, the salts of which are obtained by allowing soluble chlorides and antimony trichloride to crystallise together. The composition of these salts corresponds to various types, and it has not yet been established whether we are dealing with various complex acids or, partly, with double salts. The most frequent type is M_3SbCl_6, containing probably the trivalent anion $SbCl_6'''$.

Antimony Tribromide, $SbBr_3$, is formed with great rise of temperature on bringing the elements together. In its properties it is very similar to the trichloride and, like it, decomposes with water into basic bromide and free hydrobromic acid. The boiling point is 270°, the melting point, 95°.

Antimony Tri-iodide, SbI_3, is obtained from the elements by warming, and crystallises in three different forms whose relative degrees of stability have not yet been determined. According to the form, the colour of the crystals is dark red or green-yellow; the melting point of the form, stable at higher temperatures, is 167°, the boiling point, 400°; the vapour of the tri-iodide is of a fine scarlet colour. With water, it decomposes in the same manner as the other halogen compounds; the solution containing antimony, which is thereby produced, is coloured yellow, from which the presence of undissociated iodide in the aqueous solution can be concluded. The precipitate of oxyiodide is red to yellow in colour, and the colour is so much the brighter the smaller the amount of iodine.

Antimony tri-iodide unites with the soluble iodides to form complex salts, which belong chiefly to the type $MSbI_4$, with the anion SbI_4'.

Antimony Trifluoride, SbF_3, is a white mass similar to the trichloride, which can be dissolved in water without the separation of precipitates. This is probably due to very slight electrolytic dissociation of the fluoride. Complex salts are known with the alkali fluorides.

Antimony Trisulphide.—The compound Sb_2S_3 occurs in nature as the most widespread ore of antimony, and is called *antimony glance* (or stibnite). It is a grey substance crystallising in long needles of a metallic lustre; it readily melts, and on being heated in the air, passes into antimony oxide, the sulphur being burned.

From solutions of trivalent antimony, the trisulphide is precipitated by sulphuretted hydrogen as a yellow-red, non-crystalline substance which, on being gently heated, passes into grey, crystalline antimony sulphide. Conversely, when fused stibnite is quickly cooled, an amorphous mass is obtained which is translucent, and of a dark red colour, and becomes yellow-red on being powdered. The relation which here exists is therefore similar to that between amorphous and crystalline sulphur, the amorphous form being the less stable: the velocity of transformation, however, at the ordinary temperature is so small that it cannot be observed.

Antimony sulphide is not appreciably soluble in dilute acids; it dissolves in strong hydrochloric acid with evolution of sulphuretted hydrogen. For this reason, antimony is precipitated by sulphuretted hydrogen from acid solution, provided that the solution is dilute with respect to the acid. When antimony sulphide has been brought into solution with concentrated hydrochloric acid, and if the liquid which contains sulphuretted hydrogen is diluted, a precipitate of yellow-red antimony sulphide is obtained. The remarkable phenomenon that a precipitate (not due to hydrolysis) is produced by dilution with water, is explained by the fact that the antimony trichloride present in concentrated solution contains the antimony almost entirely in the form of an undissociated compound (p. 699); the antimonion necessary for the reaction with the sulphuretted hydrogen is formed only on dilution.

Antimony sulphide readily dissolves in the alkali sulphides, especially the polysulphides. A compound of the pentavalent series is thereby formed, when excess of sulphur is present, and the reaction will be discussed later in greater detail.

Antimony sulphide also dissolves in concentrated and hot solutions of the alkali hydroxides and carbonates; on cooling and diluting, it is again precipitated as a brown powder. This precipitate was formerly applied in medicine under the name kermes; since, however, it is a variable mixture of amorphous antimony sulphide and antimony oxide, its medicinal action varies according to the method of its preparation. The reaction which here occurs has not yet been sufficiently explained; we are dealing essentially with the formation of the alkali salts of antimony oxide (p. 699), and of the corresponding compounds of antimony sulphide, which are stable in hot, concentrated solution, whereas on cooling and on dilution, the equilibrium is again shifted in the opposite sense, *i.e.* antimony sulphide is again formed.

Use is made of the precipitation of the antimony compounds by sulphuretted hydrogen for the detection and determination of antimony. Since the amorphous precipitate, even after being dried at 100°, still contains appreciable quantities of water, it is, in quantitative determinations, converted by careful heating in an atmosphere free from oxygen (in a current of carbon dioxide), into the grey, crystalline form which is of constant composition.

The naturally occurring antimony glance is employed for the preparation of metallic antimony. The red, amorphous form is used as a dye under the name antimony vermilion; red, vulcanised india-rubber is coloured with antimony sulphide.

Complex Antimony Compounds.—Trivalent antimony has, in a very marked degree, the property, already mentioned in the case of other hydroxides, of forming complex compounds with organic substances containing several hydroxyl groups. The most important of these is the compound with tartaric acid, which yields an antimonyl tartaric acid; in contrast with the ordinary antimony compounds this compound is not dissociated hydrolytically by water, so that it can be dissolved, and the solution diluted without the separation of basic substances. The exact discussion of these compounds must be reserved for organic chemistry; they have been mentioned here because tartaric acid is employed in analytical chemistry for the purpose of preparing clear, dilute solutions of antimony salts. For this purpose, the addition of a solution of tartaric acid to the liquid is sufficient. The formation of the complex compound takes place so quickly that the desired result is attained in a few moments. From such solutions, antimony sulphide is precipitated by sulphuretted hydrogen, showing that the complex is sufficiently dissociated into its components for the solubility product of antimony trisulphide to be exceeded.

Antimony Pentachloride.—By means of oxidising agents it is possible to pass from compounds of trivalent to those of pentavalent antimony. If chlorine is passed over antimony trichloride, a heavy liquid which fumes in the air is produced; this is also obtained from antimony and chlorine by using excess of the latter. At 140° it commences to boil, and the determination of the vapour density shows that it exists in the vaporous condition for the greater part undecomposed. Chlorine is, however, very readily split off, and even when the boiling is continued, so much of it escapes that there remains a considerable residue of trichloride. On the whole, therefore, the compound behaves similarly to phosphorus pentachloride (p. 357), but is somewhat more stable.

Antimony pentachloride unites with water and forms various hydrates which, however, are formed only when a small quantity of water is used, clear solutions being then produced; when dissolved in much water, it undergoes complete hydrolysis and difficultly soluble antimonic acid is deposited. It combines with hydrochloric acid to form a fairly stable, crystalline substance, which dissolves without decomposition in a small quantity of water, and has the composition $H_5SbCl_{10} \cdot 10H_2O$.

An antimony pentabromide is not known; the existence of the pentaiodide is also doubtful.

Antimonic Acid.—Antimonic acid, $Sb(OH)_5$, or its anhydrides, is obtained by the decomposition of antimony pentachloride with much water. On account of the relation of antimony to phosphorus, one would expect the existence of an orthoantimonic acid, H_3SbO_4, a pyroantimonic acid, $H_4Sb_2O_7$, and a metantimonic acid, $HSbO_3$; in the present case, however, the differences are not nearly so clear and definite as in the case of the phosphoric acids.

The precipitate obtained from antimony pentachloride has, after being dried in the air, approximately the composition of orthoantimonic acid, and is a white powder which is very slightly soluble in water but readily dissolves in caustic potash; it yields with caustic soda an almost insoluble salt, which is formed on treating the acid with a solution of caustic soda. The composition of this salt, which is also fairly quickly formed from the other forms of antimonic acid,[1] is $Na_2H_2Sb_2O_7$; it is therefore an acid salt of pyroantimonic acid. On account of its difficult solubility it can be employed as a reagent for the detection of sodium compounds.

The reagent used for this purpose is obtained from the potassium salt of metantimonic acid, $KSbO_3$, which is formed by heating antimony with saltpetre; the oxygen of the saltpetre serves to convert the antimony into antimonic acid. On being treated with a small quantity of water, this salt is converted into the acid pyroantimonate, which serves as the reagent $2KSbO_3 + H_2O = K_2H_2Sb_2O_7$.

The various antimonic acids lose water even on very gentle warming, and are converted into antimony pentoxide, Sb_2O_5, a yellow powder which becomes darker on being heated. On being more strongly heated it loses oxygen, and a compound of the composition SbO_2 or Sb_2O_4 remains. The same substance is obtained by the oxidation of antimony with nitric acid, and forms a white residue insoluble in the acid. It was formerly called antimonious acid, but it is rather to be regarded as antimonyl antimonate, if it can be regarded as a definite compound at all; its composition varies somewhat with the temperature.

Antimony Pentasulphide and the Thioantimonates.—As was mentioned on p. 706, antimony sulphide readily dissolves in the soluble polysulphides of the alkalis and of ammonia, and from the solutions well crystallised salts can be obtained in which a compound of antimony and sulphur forms the anion. The best known of these salts is the sodium compound Na_3SbS_4, which is obtained in the form of pale yellow tetrahedra with $9H_2O$ of crystallisation, by boiling together sodium sulphide (or caustic soda), sulphur, and antimony sulphide, and allowing the filtered solution to cool. It is called *Schlippe's salt*, after its discoverer.

As is shown by the formula, it is the sodium salt of the thioantimonanion SbS_4''', which corresponds to the ion of orthoantimonic acid, but contains sulphur in place of oxygen. We have already

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[1] Owing to an unfortunate, older nomenclature, the characteristic sodium salt had been formerly called sodium *metantimonate*, and this name is sometimes found even in the present-day literature. Its use ought to be discontinued as soon as possible.

(p. 412) met with such a compound in the case of thiocarbonic acid, and the relationships which are found were explained there.

In the case of the metals grouped together in the present class, the formations of such thio-ions is a general phenomenon, and the solubility of their sulphides in alkali sulphides is due to the formation of soluble alkali salts of such thio-ions.

As in the case of the oxyacids, the higher compounds, *i.e.* those richer in sulphur, have the more strongly acid character. For this reason, antimony trisulphide is only very slightly soluble in the dilute solutions of the alkali monosulphides, but is readily soluble in the yellow solutions which contain polysulphides. In the former case a salt of thioantimonious acid would be formed; such an acid, however, does not exist, and the saline compounds corresponding to it which are formed to a certain extent in concentrated solutions, are decomposed by water. The salts of thioantimonic acid, however, are very stable, and these are immediately formed when the necessary sulphur can be obtained from the polysulphide present.

Free thioantimonic acid, H_3SbS_4, is not known. If hydrion is introduced into the solution of one of its salts, sulphuretted hydrogen and antimony pentasulphide are formed: $2H_3SbS_4 = Sb_2S_5 + 3H_2S$. The process corresponds exactly to the formation of an anhydride with separation of water, the place of water being taken by sulphuretted hydrogen in the case of the thio-acid.

The *antimony pentasulphide* which can be obtained in this way, is very similar to the amorphous trisulphide as far as external appearance is concerned. It readily decomposes into trisulphide and sulphur, so that amounts of sulphur varying with the previous treatment can be extracted from the product with carbon disulphide. It is soluble not only in the monosulphides of the alkali metals but also in the hydroxides; in the latter case, antimonate is formed in the solution along with thioantimonate, or, the salts of an antimonic acid in which only a part of the oxygen is replaced by sulphur are formed. It dissolves even in the alkali carbonates, although with somewhat greater difficulty. The pentasulphide obtained by precipitation from Schlippe's salt, is employed in medicine under the name "golden sulphur of antimony."

The solutions of the thioantimonates mostly give precipitates with the salts of the heavy metals which are practically insoluble in water and are coloured yellow, red, or black. In these compounds, as in Schlippe's salt, the trivalent thioantimonanion is combined with three units of metal.

Antimony Hydride.—The relationship of antimony to nitrogen and phosphorus is seen with especial clearness in its power of forming a gaseous compound with hydrogen, SbH_3, which, as regards its composition, belongs to the same type as ammonia and phosphoretted hydrogen. This compound, certainly, has no basic properties, but this constitutes no essential difference, since these are practically wanting even in the case of phosphoretted hydrogen.

Antimony hydride, SbH_3, is obtained by the action of acids on alloys of antimony with other metals which decompose acids, especially zinc. In this way, the antimony hydride is always obtained mixed with much hydrogen. Even when it is separated from the mixture by strongly cooling, it again undergoes partial decomposition when the separated mass is gasified, so that as a matter of fact only mixtures of antimony hydride and free hydrogen are known.

If the mixture is passed through a glass tube heated at one part, the antimony hydride decomposes at that spot, and metallic antimony is deposited as a grey-black coating, which, on being heated, runs together into drops, but cannot be readily volatilised. It differs in this respect from the "arsenic mirror," which is formed under similar conditions, and with which it could be confused. Further differences will be given under arsenic.

Antimony hydride burns with a white flame; if a piece of porcelain is held in this, unburnt antimony is deposited on it as a black soot, which is converted at the edges into white, floury-looking antimony oxide. The antimony stains can be readily distinguished from the arsenic stains formed under similar conditions, by their grey (not brown) colour.

In a solution of silver nitrate antimony hydride produces a black precipitate which contains silver and all the antimony, so that the solution contains only nitric acid and undecomposed silver nitrate.

Alloys of Antimony.—Of the various metallic mixtures for which antimony is employed, the most important is that with lead. Even fairly small quantities of antimony considerably increase the hardness of lead, and in chemical manufactures, where the chemical resistibility of lead is required along with moderately great mechanical resistibility, such alloys, called *hard lead*, are employed. Type-metal, also, which along with a comparatively easy fusibility must possess a sufficient hardness and the power of exactly filling out the mould, consists essentially of lead and antimony. Alloyed with tin, antimony yields Britannia metal, which is used for domestic utensils.

CHAPTER XXXIX

ARSENIC

General.—In accordance with its smaller combining weight, arsenic deviates still more than antimony from the type of the metals, and exhibits greater similarity to the non-metal phosphorus; at the same time the tendency to form acid compounds increases. In fact, the resemblance of arsenic to phosphorus is so great that it might also have been treated along with that element among the non-metals.

Elementary arsenic occurs in various forms, which partly recall those of phosphorus. The most stable form is a grey, crystalline mass with a metallic lustre. On being heated, arsenic does not fuse, but passes, before reaching its melting point, into a brown-yellow vapour. It can be fused by heating under pressure; it then solidifies to a steel-grey, lustrous mass with a crystalline fracture.

From the vapour density of arsenic, the molar weight is found to be 300; since the combining weight is taken as 75, arsenic vapour has the formula As_4. In this respect, also, there is a similarity to phosphorus (p. 353) and a dissimilarity to the metals, in the case of which the molar weight coincides with the combining weight.

If the vapour of arsenic is quickly cooled, *amorphous arsenic* is produced, various kinds of which are known. The most interesting of these is obtained by very rapid and powerful cooling; it is yellow non-metallic, and is soluble in carbon disulphide; it rapidly undergoes oxidation in the air with faint luminescence, and emits a smell o garlic; in short, it is very similar to white phosphorus.

At the same time, other kinds of amorphous arsenic are formed more especially a velvet-black and a grey variety. All these forms are unstable, and are rapidly converted, especially when warmed, into stable, crystalline arsenic. Their formation affords fresh examples o the principle that the unstable forms are produced before the stable.

That as a rule, only the crystalline form appears to be formed from the vapour, is due to the fact that the phosphorus-like arsenic first produced changes almost instantaneously into the more stable form. Only when the velocity of this change is diminished to a small value by rapid cooling at a low temperature, can the unstable form first produced be observed.

Arsenic Trioxide.—When arsenic is heated with access of oxygen it burns with a brilliant white flame, forming an oxygen compound to which, in accordance with its composition and vapour density, the formula As_4O_6 must be assigned. For it contains 24 parts of oxygen to 75 parts of arsenic, and its vapour density yields the molar weight 396. Strictly speaking, therefore, this compound would have to be called arsenic hexoxide, but one has become accustomed to write the formula As_2O_3, and to call the substance arsenic trioxide. In ordinary life, in which this compound plays a certain rôle, it is called white arsenic or simply arsenic.

Arsenic trioxide occurs in various forms. When manufactured on the large scale it appears in the first instance as a transparent glass, which is generally coloured slightly yellow by traces of impurities. This glass is *amorphous* arsenic trioxide. On being kept some time, the glass becomes milk-white and looks like porcelain; since this change is accelerated by the moisture in the air it proceeds from the outside towards the interior. On breaking a moderately large piece, therefore, which has on all sides assumed a porcelain-like appearance, a kernel of unchanged glassy substance is frequently found in the nterior. The porcelain-like mass is *crystalline* arsenic trioxide. Since his is produced spontaneously from the amorphous form, it is the nore stable of the two, and in accordance with a general law (p. 259) t is in all solvents less soluble than the amorphous form. When, herefore, water is in contact with the two forms the solution which s saturated in respect of the amorphous form will be supersaturated n respect of the crystalline form. The amount of the latter will herefore increase from the solution; this becomes unsaturated in espect of the amorphous form, dissolves fresh quantities of it, and deposits it as crystals. This process is continued until all the morphous substance is converted into crystalline. This furnishes he explanation of the accelerating influence of moisture on the ransformation (cf. p. 666).

Larger crystals of arsenic trioxide are obtained by dissolving the ubstance in warm hydrochloric acid. On cooling, it separates out ery slowly and forms regular octahedra with a diamond-like lustre. Well-formed crystals can also be obtained by sublimation. Arsenic rioxide, like metallic arsenic, also passes without fusion into vapour.

* Besides the regular form of arsenic trioxide, a rhombic form lso exists. It occurs (rarely) in nature, and as a mineral it is called audetite. The stability relations of the two crystalline forms have ot yet been determined.

In the manufactures, arsenic trioxide is obtained by roasting senical ores. The trioxide is collected by leading the vapours roduced through chambers and passages of masonry in which the trioxide is deposited as a powder known as "poison-flour." This i purified by resublimation from iron pots having cylinders placed ove them, and is thereby obtained in the glassy form.

Arsenic trioxide is only sparingly soluble in water. On placin the powder in water it is not wetted, and owing to the surface tension it remains floating on the water although its density is 3·7.

Arsenic trioxide readily loses oxygen. In order to show this, small glass tube is drawn out to a point and fused off; a particle o arsenic trioxide is then placed in the point and above it a small piec of freshly ignited wood-charcoal. If the tube is so heated that th charcoal is first caused to glow and then the arsenic trioxide volatilised the latter loses its oxygen in contact with the charcoal and the liberate arsenic is deposited as a black coating on the colder portions of th tube. This "arsenic mirror" can be easily recognised by its feebl metallic lustre and the brown colour which it shows in thin layers b transmitted light. By means of this experiment, very small quantitie of the trioxide can be detected with certainty.

When greatly diluted, arsenic trioxide is used as a medicament It is remarkable, also, that the organism of man and the animals ca gradually become accustomed to large quantities of arsenic. By mean of it horses acquire a healthy and spirited appearance, and arseni eaters also assert that they can undergo much more bodily exertio under the influence of this substance. The organism accustomed t arsenic, however, rapidly decays when the use of this substance i interrupted, and it can be kept in an active condition only by regula or increased doses of the poison.

Arsenious Acid.—The aqueous solution of arsenic trioxide has feebly acid reaction, and contains an acid which is formed from th trioxide by the addition of the elements of water. In all probability a decomposition takes place in the process, so that the acid contain only two combining weights of arsenic. Which of the variou hydrates $H_6As_2O_6$, $H_4As_2O_5$, $H_2As_2O_4$ *predominates* in the solution (fo we must assume that all are present, although in very varying amount is unknown; by reason of the very feebly developed acid properties the formula $H_2As_2O_4$ will be the most suitable expression of th properties.

The electrolytic dissociation of arsenious acid is extremely small its soluble salts are therefore dissociated hydrolytically to an appreci able extent, and the alkali salts, more especially, have an alkalin reaction. The salts of the other metals correspond to the orthoaci $H_6As_2O_6$, and are mostly very slightly soluble in water. This is tru more especially for the ferric salt, so that freshly precipitated ferri hydroxide by combining with the arsenious acid can be used as a effective antidote in cases of poisoning with this substance. Th copper salt is green and is employed as a colouring matter (Scheele green). With copper acetate, copper arsenite forms a double salt of brilliant green colour, which is applied under the name Schweinfurter green. On account of their containing arsenic, both substances are dangerous, and their use for articles of daily use, and more especially also in wall-papers, must by all means be excluded.

Arsenic Trichloride.—In a current of chlorine, arsenic burns without external application of heat and forms a colourless, heavy liquid (density 2·2), which boils at 134° and whose vapour yields the molar weight 182. The latter number forms the chief reason for assigning to arsenic the combining weight 75, and to its chloride the formula $AsCl_3$, for 75 is the smallest weight of arsenic occurring in a mole of any volatile arsenic compound.

Arsenic trichloride can also be obtained by pouring sulphuric acid over arsenic trioxide and adding pieces of rock salt. By the action of the sulphuric acid on the sodium chloride, hydrochloric acid is formed, and this acts on the arsenic trioxide according to the equation $As_4O_6 + 12HCl = 4AsCl_3 + 6H_2O$. Since, on the other hand, arsenic trichloride is partially converted by water into trioxide and hydrochloric acid, the method is successful only when a large excess of concentrated sulphuric acid is employed whereby the water produced is bound.

A chemical equilibrium, which depends on the concentration of the four substances, exists between water, arsenic trichloride, hydrogen chloride, and arsenic trioxide. An increase of the water promotes the decomposition of the trichloride; an increase of hydrogen chloride, its re-formation. That ordinary aqueous hydrochloric acid also converts part of the trioxide into chloride, is seen from the increased solubility of the trioxide in concentrated hydrochloric acid as compared with that in water; the excess is dissolved as chloride.

The presence of the chloride in the hydrochloric acid solution is also made evident from the fact that on distillation an arsenical distillate is obtained. Since arsenic trioxide or arsenious acid is not volatile under these conditions, the arsenic can pass into the distillate only in the form of volatile trichloride. This behaviour is of importance for the treatment of arsenical substances in analysis. Solutions containing arsenious acid and hydrochloric acid cannot be evaporated without a danger of loss of arsenic.

* In order to avoid this we may either make the liquid alkaline before evaporating it, or the arsenious acid may be converted by an oxidising agent into arsenic acid. A solution of the latter can be evaporated without loss even when strongly acidified with hydrochloric acid. For arsenic does not form any pentachloride corresponding to arsenic acid, nor any other volatile chlorine compound belonging to this stage of oxidation.

* The above gives a means of purifying sulphuric acid containing arsenic. The arsenic is reduced to arsenious acid (if it is not already in this condition), and hydrogen chloride is passed through the heated acid; the arsenic is then volatilised as the trichloride.

* Conversely, hydrochloric acid can be freed from arsenic by oxidising the latter to arsenic acid and distilling the acid. The arsenic remains in the residues.

Arsenic forms similar compounds with bromine and iodine, $AsBr_3$ and AsI_3; these have a higher boiling point and melting point. At room temperature they are both solid; the bromide melts at 25° and boils at 220°; the melting point and boiling point of the iodide are not definitely known, but they are both higher than in the case of the bromide.

The compounds are obtained by bringing together the free elements; this is best done under carbon disulphide, which can then be removed by evaporation. The bromide is colourless, the iodide red. Like the chloride, both compounds are decomposed by water; the relative amount of the portion dissolving without decomposition is not known.

Arsenic Trisulphide.—Arsenic trisulphide, As_2S_3, corresponding to the trioxide, occurs in nature. It forms yellow crystals with a slight metallic lustre; on being ground it yields a bright lustrous powder, which was formerly used as a pigment. To this the name *orpiment*, the mineralogical name for arsenic trisulphide, is due. Arsenic trisulphide is obtained as a sulphur-yellow powder, practically insoluble in water, by precipitating acid solutions of arsenious acid with sulphuretted hydrogen. Since this is the way in which arsenic is ordinarily separated in analytical operations, it is important to know the exact properties of arsenic trisulphide.

On treating a dilute solution of arsenious acid in pure water with sulphuretted hydrogen, the smell of the gas disappears; no precipitate is formed, but the solution becomes yellow. If a cone of convergent light rays is allowed to fall on the liquid, the path of the light becomes bright, owing to diffusion. This fact (and the polarised condition of the diffused light) shows that the arsenic trisulphide in the liquid is not really in solution, but is in suspension in a state of very fine division. The particles are, however, so small that they are neither visible under the microscope nor are retained by filter paper. Their size is of the order of a wave-length of light.

If some hydrochloric acid is added to the liquid it becomes turbid, and in a few moments arsenic trisulphide separates out in yellow flakes. Other substances, acids and neutral salts, act in the same manner as hydrochloric acid, and in a way that is fairly independent of their chemical nature. If the precipitate is placed as quickly as possible after its separation on a filter and the acid washed away with pure water, it again partly passes into a liquid as before; another portion remains insoluble. If the precipitate is allowed to remain some time in the solution in which it was formed, it becomes completely insoluble. We again recognise here the properties of *colloidal solutions* (p. 420). The formation of such colloidal solutions takes place most easily in pure water. Addition of foreign substances, especially of a saline character (to which free acids and bases also belong) causes the separation of the colloidal substances in the form of amorphous flakes. For this reason the colloidal solution of arsenic trisulphide can be obtained with sulphuretted hydrogen only from a pure solution of arsenious acid. If the solution contain, for example, hydrochloric acid along with the arsenious acid, the arsenic trisulphide is at once formed as a flocculent precipitate on being treated with sulphuretted hydrogen.

If the yellow colloidal solution is kept some time it becomes more and more turbid, and gradually deposits more and more of the arsenic trisulphide as a precipitate. This is also a general property of colloidal solutions; the dissolved substance passes in time spontaneously into an insoluble form.

The characteristic difference between colloidal solutions and the true solutions, viz. that the former do not exhibit any elevation of the boiling point nor depression of the freezing point as compared with pure water (p. 421), is also found in the case of colloidal arsenic trisulphide.

Arsenic trisulphide, not in the colloidal condition, is practically insoluble in water and acids; more especially, it is not attacked by fairly concentrated hydrochloric acid, and thereby differs essentially from antimony trisulphide. It is readily oxidised by nitric acid to arsenic acid and sulphuric acid. On standing in a moist condition in contact with the oxygen of the air, it is converted fairly quickly into soluble arsenious acid.

Arsenic trisulphide is readily soluble in alkaline liquids of all kinds, caustic alkalis, alkali carbonates, ammonia, and also ammonium carbonate; it also dissolves in soluble sulphides and hydrosulphides. Various salts are contained in the solutions according to the solvents used; these may be regarded as arsenites in which some or all of the combining weights of oxygen are replaced by sulphur. We are therefore dealing with the salts of thioarsenious acid, and the members intermediate between these and the salts of arsenious acid. In the latter case we are dealing with mixtures the nature of which has not yet been explained. Arsenic trisulphide is again precipitated from all these solutions by the addition of acids.

By means of its solubility in ammonium carbonate arsenic trisulphide can be readily separated from all the other sulphides which are precipitated from acid solution by sulphuretted hydrogen.

Arsenic Hydride.—When a solution containing arsenic (*e.g.* arsenious acid) is added to a mixture of zinc and hydrochloric acid, from which hydrogen is being evolved, a gaseous compound mixes with the hydrogen, and essentially alters its properties. The arsenical hydrogen has a strong garlic-like smell, is extremely poisonous, and burns with a bright white flame, which differs essentially from the pale blue flame of pure hydrogen.

The cause of this change is the formation of *arsenic hydride*, AsH_3, which can be obtained in an approximately pure condition by fusing together arsenic and zinc to form the compound Zn_3As_2, and decomposing this with hydrochloric acid: $Zn_3As_2 + 6HCl = 2AsH_3 + 3ZnCl_2$. In the pure state, arsenic hydride is a colourless gas, which liquefies at − 40°.

The presence of arsenic hydride along with much hydrogen can be recognised not merely by the peculiarities above mentioned. If the dried arsenical gas is passed through a glass tube constricted at one point, and the latter heated to a low red heat immediately in front of the constriction, the arsenic hydride decomposes into hydrogen, which escapes, and metallic arsenic, which is deposited as an "arsenic mirror" (p. 708) in the constricted portion of the tube. The arrangement is shown in Fig. 120.

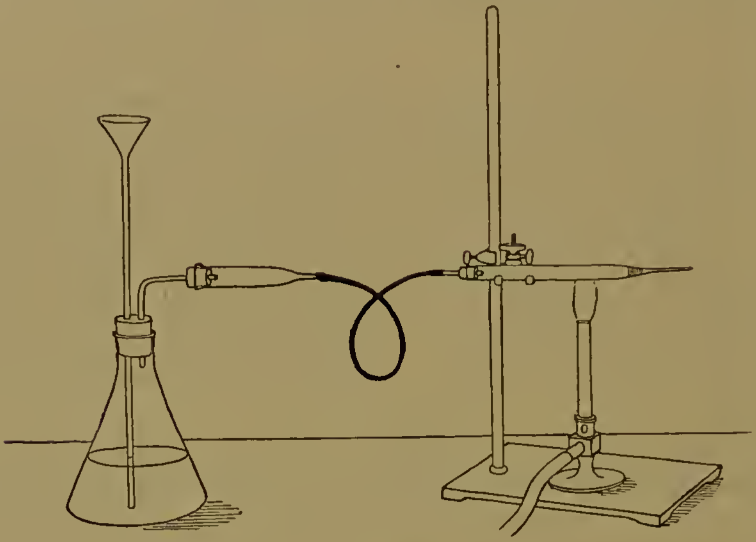

FIG. 120.

Since, in this way, all arsenic compounds dissolved in acid liquids can be converted into arsenic hydride or metallic arsenic, and even extremely small quantities of the latter can be recognised in the form of the mirror, the above arrangement is used for the detection of arsenic in analysis.

The flame of the arsenical hydrogen is white, and deposits on cold objects held in it a brown-black film of metallic arsenic. A black precipitate is produced in a silver solution.

All these reactions are very similar to those of antimony hydride (p. 705), and it is therefore of importance to distinguish between the two. For this purpose a solution of sodium hypochlorite may be most simply used. In this the arsenic mirror speedily dissolves, while the antimony mirror remains for a long time unchanged. Further, the arsenic mirror is readily volatile, the antimony mirror is not.

Sulphuretted hydrogen or ammonium sulphide vapour converts the former into bright yellow arsenic sulphide, insoluble in hydrochloric acid, the latter into yellow-red antimony sulphide, soluble in hydrochloric acid. The precipitate produced in silver solutions by arsenic hydride is silver, the arsenic passing into solution as arsenious acid. Antimony hydride forms silver antimonide, and there is no antimony in solution. The last reaction affords a means of analysing mixtures of the two hydrogen compounds.

Compounds of Pentavalent Arsenic.—The compounds hitherto discussed can all be referred to the trivalent type. Besides the latter, arsenic forms two other series of compounds, one of which corresponds to the pentavalent type, while there are also other compounds which point to the existence of a divalent type. The latter are comparatively rare and unimportant.

When arsenic trioxide is treated with oxidising agents, *e.g.* nitric acid, a solution is obtained from which, on greatly concentrating, *arsenic acid*, H_3AsO_4, crystallises out.

In its whole behaviour arsenic acid is very similar to orthophosphoric acid. Like this it is tribasic, but its soluble, normal salts are partially hydrolysed on being dissolved in water, and therefore react alkaline. All the salts of arsenic acid are isomorphous with the corresponding salts of phosphoric acid; in fact, it was in the case of the arsenates and phosphates that similarity of form along with corresponding composition was first observed.

The solubility relations of the salts of arsenic acid have also a very great similarity to those of the salts of the phosphoric acids.

The following differences, however, exist in the behaviour of the two substances. In the first place, one has not succeeded in preparing partial anhydrides of arsenic acid, corresponding to pyrophosphoric and metaphosphoric acids. On the contrary, only orthoarsenic acid, H_3AsO_4, along with its salts, and arsenic pentoxide are known.

Further, even on being gently warmed, arsenic acid loses water and passes into its anhydride, arsenic pentoxide, As_2O_5; while phosphoric acid (p. 364) can be dehydrated, by heating, only to metaphosphoric acid.

Arsenic pentoxide is obtained as a white powder by heating arsenic acid to a moderate temperature. On being more strongly heated it loses oxygen, and passes into arsenic trioxide. When mixed with water it first forms a pasty mass, which is slowly converted into a clear solution of arsenic acid.

Arsenic acid is used in the arts and manufactures as a feeble oxidising agent in the preparation of certain dyes.

The *salts* of arsenic acid are of slight importance. While those of the alkali metals are readily soluble in water, the other metals mostly form difficultly soluble salts. The magnesium ammonium compound, $Mg(NH_4)AsO_4$, which is formed under similar conditions to the corresponding phosphate (p. 536), and, similarly to it, is used for the determination of arsenic acid, and therefore also of arsenic, deserves to be mentioned. Under the action of reducing substances (filter paper, unburnt coal-gas) and on warming, reduction very readily occurs with volatilisation of arsenic, and attention must be paid to this in analysis.

In respect of its electrolytic dissociation, arsenic acid is very similar to phosphoric acid. Even up to a great dilution the aqueous solution contains chiefly the ions $H^{\cdot}$ and H_2AsO_4', and the further stages of dissociation are quite subsidiary. At the same concentration arsenic acid is less dissociated than phosphoric acid, but the difference is not great.

An arsenic pentachloride corresponding to arsenic acid is not known. This is somewhat remarkable, since its congeners both with lower and higher combining weight, viz. phosphorus and antimony, each form a pentachloride. In the case of bismuth, certainly, which follows antimony, a pentachloride is also unknown.

Arsenic Pentasulphide.—A solution of sodium thioarsenite, Na_3AsS_3, when warmed with sulphur, readily takes up a combining weight of the latter, and forms a new salt according to the equation $Na_3AsS_3 + S = Na_3AsS_4$. We are here again dealing with the sodium salt of a thio-acid, H_3AsS_4. Since the formula corresponds to that of arsenic acid, H_3AsO_4, the acid is called thioarsenic acid.

On attempting to liberate the thioarsenic acid by the addition of another acid, a yellow precipitate is produced, which looks almost like arsenic trisulphide, but has the composition As_2S_5, and is therefore arsenic pentasulphide. In this process again thioarsenic acid is first formed, but the acid is not stable, and decomposes into arsenic pentasulphide and sulphuretted hydrogen.

Arsenic pentasulphide is also a rather unstable compound, and readily decomposes into arsenic trisulphide and sulphur.

Compounds of the Divalent Type.—Arsenic unites with sulphur and with iodine to form the compounds As_2S_2 and AsI_2, which belong to a lower type than the compounds hitherto discussed.

The sulphur compound occurs naturally in dark red crystals, and can be prepared from the two elements by fusing them together. Its mineralogical name is *realgar*. It fuses readily, and burns in the air to arsenic trioxide and sulphur dioxide; it dissolves in the solvents for arsenic trisulphide, leaving behind a residue of arsenic.

Arsenious iodide, AsI_2, is also obtained as a dark-red mass by heating its constituents in a closed tube, and crystallises from carbon disulphide in long needles. In chemical reactions it behaves similarly to the sulphur compound, metallic arsenic being deposited and the corresponding trivalent compounds formed.

CHAPTER XL

VANADIUM, NIOBIUM, TANTALUM, GALLIUM, AND INDIUM

Vanadium.—The three elements, vanadium, niobium, and tantalum resemble those of the nitrogen group in that they chiefly form compounds belonging to the pentavalent type, and that their higher oxygen compounds have an acid character. In the elementary state they have the properties of metals; their halogen compounds are readily volatile. All three are only sparingly found in the earth's crust, although the first mentioned, vanadium, occurs in small quantities widely distributed.

Vanadium is obtained from the mixtures containing it by fusing these with soda and saltpetre. It is thereby converted into soluble sodium vanadate, and can be extracted with water. After the admixtures have been removed as far as possible, pieces of solid ammonium chloride are placed in the liquid. Ammonium vanadate is then formed, which is practically insoluble in the concentrated solution of ammonium chloride, and separates out as a crystalline powder. By heating the ammonium salt in the air vanadium pentoxide, V_2O_5, the anhydride of vanadic acid, is obtained as a yellow or brown powder, which dissolves in water with a red colour. The solution appears, however, to be essentially of a colloidal nature, as it is precipitated by neutral salts.

Various acids can be derived from vanadium pentoxide. Metavanadic acid, HVO_3, in the form of its salts, is the best known. The above-mentioned ammonium salt is a metavanadate $(NH_4)VO_3$. Ortho- and pyro-vanadates also exist. Besides these acids, "condensed" acids, containing several combining weights of vanadium, are readily formed. Thus, for example, the salts of tetravanadic acid, $H_2V_4O_{11}$, and of hexavanadic acid, $H_2V_6O_{16}$, are known. They are formed on acidifying the simple vanadates, and are of a yellow-red to dark-red colour, while the simple vanadates are white, or sometimes yellow. Little is known, however, of the conditions of formation and of mutual transformation of these various forms.

Vanadium pentoxide is capable also of uniting with strong acids to form salt-like compounds, hydroxyl being split off instead of the acid hydrogen. Such compounds, more especially with sulphuric acid, are known even in the solid state.

By reducing the pentoxide with hydrogen, or with charcoal at a high temperature, vanadium trioxide, V_2O_3, is obtained as a grey-black powder with metallic lustre. This was formerly regarded as metallic vanadium, since, besides having a metallic lustre, it is also a good conductor of electricity. It dissolves in acids to form dark-green salts, which are also obtained by reducing acid solutions of the pentoxide with zinc.

Besides these two oxides, the compounds V_2O, V_2O_2, V_2O_4, and some intermediate compounds have also been prepared. They have all a metallic appearance. The dioxide dissolves in dilute acids to form blue liquids, which evolve hydrogen, and have strong reducing properties.

The compounds with the halogens, especially with chlorine, exhibit as great variety as the oxygen compounds. Strange to say, a pentachloride, which would be expected, corresponding to the pentoxide, does not exist; the highest chloride stage is the tetrachloride, VCl_4. An oxychloride, however, viz., vanadyl chloride, $VOCl_3$(VO = vanadyl), belonging to the pentavalent type, is known. It is obtained by first passing hydrogen and then chlorine over a heated mixture of vanadium pentoxide and charcoal. It is a bright yellow liquid, boiling at 127°, which reacts with water with great rise of temperature, and fumes in the air. From this $VOCl_2$ and $VOCl$ are obtained by reduction with hydrogen; they are both solid, crystalline substances, the former being green, the latter brown.

If a mixture of vanadyl trichloride vapour and chlorine is passed over red-hot charcoal, the tetrachloride, VCl_4, is obtained as a brown liquid, boiling at 154°. On being more strongly heated it decomposes into chlorine and vanadium trichloride, VCl_3, which forms lustrous, violet-red crystals, which recall chromic chloride. They attract moisture from the air and deliquesce to a brown liquid. On heating the vapour with hydrogen the tetrachloride is converted into vanadium dichloride, VCl_2. This forms apple-green, difficultly volatile crystals with a micaceous lustre, which deliquesce in the air to a violet-blue liquid.

Finally, on strongly heating the dichloride in a current of hydrogen, metallic vanadium is obtained as an unmelted, grey mass, which acquires a metallic lustre on being rubbed, and does not dissolve in dilute acid. It burns readily in a current of nitrogen, forming vanadium nitride, VN, a yellow-brown powder with a metallic lustre. On fusion with caustic potash the nitride is converted into vanadic acid with evolution of ammonia.

On passing sulphuretted hydrogen into a solution of ammonium vanadate in ammonia a precipitate is produced which, on continuing to pass the gas, dissolves, forming a fine, violet-red coloured liquid. From this solid ammonium thiovanadate, resembling potassium permanganate in appearance, crystallises out. The salt has the composition $(NH_4)_3VS_4$, and therefore belongs to the ortho series. On adding acids, sulphuretted hydrogen is evolved, and a brown precipitate is formed, which, however, does not appear to be pure vanadium pentasulphide. The latter is obtained as a black powder by fusing the trisulphide with sulphur. The trisulphide, in its turn, is obtained by heating the pentoxide in a current of sulphuretted hydrogen, or, better, of carbon disulphide. It is grey-black in colour, and dissolves in alkali sulphides, especially in such as contain excess of sulphur, forming a red-violet solution of thiovanadate.

Vanadic acid has the property of catalytically accelerating certain oxidation processes (*e.g.* the oxidation of aniline to aniline black, with sodium chlorate), and is therefore employed for such purposes in the arts and manufactures. Even very small quantities of the acid are sufficient to effect a great acceleration.

The combining weight of vanadium has been found equal to 51·2.

Niobuim and **Tantalum** are two extremely rare elements, whose combining weights are respectively 94 and 183. Free niobium is obtained as a grey metal by the reduction of its chloride with hydrogen at a red-heat. It resists the action of dilute acids, but burns in a current of chlorine. With oxygen, niobium forms a pentoxide, Nb_2O_5, which is the anhydride of a very weak acid, the alkali salts of which are decomposed even by carbonic acid, with precipitation of the hydroxide. On being heated in a current of hydrogen the pentoxide passes into a black, metal-like dioxide, which was formerly taken for the metal.

With chlorine, niobium forms a pentachloride which can be obtained by heating the pentoxide with charcoal in a current of chlorine. It forms yellow crystals which melt at 194° and boil at 240°. If in the preparation the presence of water is not avoided, niobium oxychloride, $NbOCl_3$, is chiefly formed as a white mass, which does not fuse, but sublimes at 400°. A trichloride is also known, which is deposited on strongly heating the vapour of the pentachloride.

Niobium forms complex compounds with fluorine, which exhibit a somewhat varied composition, and which have not yet been arranged under simple types.

The compounds of **tantalum** are very similar to those of niobium. Especially characteristic is potassium fluotantalate, the potassium salt of hydrofluotantalic acid, H_2TaF_7; the latter is readily formed by dissolving the pentoxide in hydrofluoric acid.

Gallium and Indium.—The elements most nearly related to these two rare elements are to be found among the alkaline earth metals. In certain respects, however, they resemble the heavy metals, so that it appeared more suitable to treat of them at this point.

Gallium occurs very sparingly in certain zinc blendes, and was discovered by means of the spectroscope by Lecoq de Boisbaudran in

1875. With the exception of mercury, it is the only metal which can be liquid at the ordinary temperature. Its melting point, it is true, lies somewhat higher, viz. 30°, but it can easily be supercooled, and it remains liquid at room temperature if not brought into contact with the solid metal. It has the density 6, and is, in the solid state, hard and brittle. It undergoes superficial oxidation in the air and in water, and readily dissolves in acids and alkalis with evolution of hydrogen.

Gallium has the combining weight 69·9.

Gallium yields two series of compounds, in which it appears as divalent and as trivalent. The first series has been little investigated, and the corresponding compounds are converted by water into compounds of the trivalent series with evolution of hydrogen.

The derivatives of the trivalent series are derived from the trivalent trigallion, $Ga^{\cdot\cdot\cdot}$. This is colourless, is only slightly basic, and in its properties is closely related to aluminion. Its salts, however, undergo hydrolysis more readily. Gallium hydroxide, which can be obtained by the careful addition of a base to gallic salts, is a gelatinous, white precipitate, which dissolves both in acids and in bases. It is appreciably soluble also in ammonia, showing that gallium hydroxide has somewhat stronger acid properties than aluminium hydroxide, and can therefore form anions of the composition GaO_3H_2', GaO_3H'', GaO_3'''.

Gallium unites with chlorine to form a sub-chloride, $GaCl_2$, which is formed from the metal and free chlorine, using excess of the former. It is a white mass which melts at 164° and boils at 535°. When once fused it remains for a long time liquid, even at room temperature, since by reason of the rarity of the element the presence of particles of it in the dust is excluded. With water it yields a basic chloride and hydrogen.

Gallic chloride is formed in the same way as the gallous chloride, if excess of chlorine is employed. It melts at 76° and boils at 220°. The vapour density leads to a molar weight between 350 and 190, and shows, therefore, that the vapour is a mixture of Ga_2Cl_6 and $GaCl_3$, the composition of which depends on the pressure and temperature (cf. p. 324). The chloride dissolves in water, but soon deposits basic compounds, hydrochloric acid being split off.

The other gallic salts behave in a similar manner. Mention should be made of the sulphate, which is similar to aluminium sulphate, and also forms alums, which crystallise in the usual regular forms, with the alkali sulphates.

Indium was discovered in 1863 by Reich and Richter, also by means of the spectroscope, and is, like gallium, associated with zinc in certain blendes.

Metallic indium is soft, like lead, white-grey in colour, has the density 7·4, melts at 176°, is oxidised in the air, and stands between cadmium and lead in the potential series. Its combining weight is 113·7.

In its compounds indium appears as mono-, di-, and tri-valent, but the last class of compounds are alone stable in aqueous solution. The former are represented by the chlorine compounds InCl and $InCl_2$, the latter of which is obtained by heating the metal in a current of chlorine. It is obtained as a yellow liquid, which solidifies to a white crystalline mass. This dissolves in water with formation of indium trichloride, a third of the indium separating out as the metal. If the dichloride is fused together with metallic indium, the latter dissolves with a dark-red colour, and yields a black-red crystalline substance, indium monochloride; this is also decomposed by water into metallic indium, which is deposited, and indium trichloride, which passes into solution.

Indium trichloride is formed as a white mass by the action of excess of chlorine on metallic indium; it volatilises at about 440° and dissolves in water with great rise of temperature. The aqueous solution is fairly stable, and can be evaporated on the water-bath without material decomposition. With hydrochloric acid it forms a complex hydrochloroindic acid, H_3InCl_6, which is known in the form of its good crystallising alkali salts.

From feebly acid solutions, sulphuretted hydrogen precipitates yellow indium sulphide, which is soluble in strong acids.

From the solutions of indium chloride, bases precipitate the white hydroxide, $In(OH)_3$, which looks like alumina, and on ignition leaves a greenish-yellow residue. The hydroxide is not soluble in excess of ammonia, but is so in excess of alkalis. On boiling the solution hydroxide is again precipitated; the reason of these phenomena has already been explained (p. 546).

Regarding the salts there is not much to say; the sulphate forms a regular alum with potassium or ammonium suphate.

The "basic indium sulphite," of the composition $In_2(SO_3)_3 + In_2O_3 + 8H_2O$, is of importance in analysis. It is deposited as a very difficultly soluble precipitate when the solution of an indium salt is boiled with acid sodium sulphite. We are probably dealing here with a complex compound; nothing is known, however, regarding its constitution.

CHAPTER XLI

TIN AND ITS CONGENERS

General.—Just as in bismuth we met with a metal of pronounced metallic character connected by a regular transition with the decidedly non-metallic elements nitrogen and phosphorus, so we have in tin a metal whose extreme congeners are to be found in silicon and carbon. In this case also the intermediate members exist by which the union between such different end-members is effected.

Tin is a white metal which has been known from olden times; it has a low melting point (235°), and is very stable towards air and water at the ordinary temperature. It is not found in the free state on the earth's surface, but only as the oxide; it can, however, be so easily reduced with charcoal that the early knowledge of it is readily explicable.

Metallic tin has the density 7·3, and solidifies in a crystalline condition on cooling. This character quickly disappears when the metal is rolled, and tin can be beaten out to thin leaves; this is greatly used, under the name of *tinfoil*, for preventing the volatilisation of volatile substances and protecting substances, which are acted on by the air, from oxygen. The metallic surface keeps very well so long as the temperature is not raised; the simultaneous action of air and water has also very little influence on the metal, so that vessels made of tin (or coated with tin) are greatly used in the household, in drug stores, and in the laboratory. In the preparation of distilled water in the laboratory, more especially, the water vapour is condensed in tin spirals, since water does not dissolve an appreciable quantity of this metal.

Besides the ordinary white tin, a grey form is also known, which has a much smaller density (5·8), and which, under certain conditions, is formed from white tin. It has been found that we are here dealing with an enantiotropic form, which is stable at lower temperatures, while white tin is stable at higher temperatures. The transition temperature is 20°. In spite of the fact, therefore, that at medium temperatures ordinary white tin is in the metastable region, the formation of grey tin rarely occurs, since in the neighbourhood of the point of transition the velocity of transformation is very small. On lowering the temperature, this velocity first increases and then decreases. The increase is due to the fact that in general transformation takes place all the more quickly the further the substance is removed from the point of equilibrium. On the other hand, the general diminution of the reaction velocity by lowering of temperature comes into play, and the result is that on continuously lowering the temperature the velocity of transformation first increases and then decreases. In the case of tin the temperature of greatest velocity is about − 48°; the formation of grey tin has, therefore, been observed chiefly in great cold.

At a moderately high temperature tin oxidises fairly quickly and passes into its dioxide. It is only slightly attacked by dilute acids. Concentrated hydrochloric acid dissolves it with evolution of hydrogen, nitric acid oxidises it to insoluble dioxide. In the potential series it stands between cadmium and lead.

Tin forms two series of compounds, in which it is respectively divalent and tetravalent; the former are called stannous, the latter stannic compounds. In the divalent series it forms a divalent distannion, $Sn^{\cdot\cdot}$; the oxide of the second series is an acid anhydride.

Distannion. — Salts of distannion can be obtained only with difficulty by dissolving tin in dilute acids. The most easily formed is the chloride, $SnCl_2$, which is almost the only fairly well-known stannous salt. Distannion is colourless, and has a poisonous action.

From solutions of the stannous salts soluble bases precipitate white stannous hydroxide, which readily dissolves in an excess of caustic potash or soda, but is insoluble in ammonia. On being heated the alkaline solution deposits metallic tin, a salt of stannic acid, belonging to the tetravalent type, being formed. The reaction corresponds exactly with the transformation of monocuprion into dicuprion and metallic copper (p. 640). In other respects also the solution is unstable; on keeping it at room temperature black stannous oxide, SnO, the anhydride of stannous hydroxide, is deposited. The latter is much less soluble than the hydroxide, and the hydrolysis which the alkaline solution experiences is sufficient to cause the separation, not indeed of the soluble hydroxide, but of the oxide. The case is exactly similar to that of beryllium oxide (p. 546).

The stannous salts readily pass into stannic compounds, and are therefore strong reducing agents. They precipitate the noble metals from their solutions; mercuric chloride is first reduced to mercurous chloride, forming a white precipitate, and then to a grey powder of metallic mercury. This very sensitive reaction is employed for the detection both of mercury and of the stannous salts. The oxygen of the air is also quickly absorbed. Solutions of stannous salts quickly become turbid in the air, difficultly soluble oxidation products being deposited. Oxidation is avoided as far as possible by introducing a little metallic tin into the acid solution, whereby any stannic compound which is formed is again reduced.

Stannous chloride crystallises with two moles of water of crystallisation in readily soluble needles, which are generally superficially oxidised, and do not therefore yield a clear solution. This chloride is known commercially as *tin salt*, and is used as a mordant in dyeing and also as a reducing agent in the manufacture of organic compounds.

Hydrochloric acid combines with stannous chloride to form hydrochlorostannous acid, of which probably several exist, the chief being $HSnCl_3$ and H_2SnCl_4. The corresponding alkali salts are known; they crystallise well, and prove to be more stable than stannous chloride.

Stannous bromide is very similar to the chloride. *Stannous iodide* is a red crystalline substance which is difficultly soluble in water, but which dissolves in hydriodic acid and soluble iodides, forming with these complex salts of iodostannosion, SnI_4''. Water decomposes them, oxyiodides being deposited and hydriodic acid passing into solution.

In the solutions of the stannous salts sulphuretted hydrogen produces a brown-black precipitate of *stannous sulphide*, SnS, which is not soluble in dilute acids. Strong hydrochloric acid dissolves it with evolution of sulphuretted hydrogen.

It is not dissolved by alkali sulphides if these do not contain an excess of sulphur, and are therefore colourless; it dissolves, however, in alkali polysulphides, whereby a simultaneous change into the stannic series occurs and a thiostannic acid is formed. This is seen from the fact that acids no longer precipitate from these solutions black-brown stannous sulphides but yellow stannic sulphide.

The Stannic Series.—It is not quite certain whether in the solutions of the salts of the stannic series the presence of a tetravalent stannion $Sn^{\cdot\cdot\cdot\cdot}$ in any considerable quantity has to be assumed. Stannic hydroxide behaves chiefly as a very weak acid, and the solutions of the corresponding halogen compounds undoubtedly contain a considerable portion of the compound in the undissociated state. Since, however, stannic hydroxide also dissolves in other acids, *e.g.* sulphuric acid, one may assume the presence of cations derived from $Sn(OH)_4$, although the first stages of the electrolytic dissociation, viz., the cations $Sn(OH)_3^{\cdot}$, $Sn(OH)_2^{\cdot\cdot}$, and $Sn(OH)^{\cdot\cdot\cdot}$, will predominate.

When tin is heated in a current of chlorine it combines with the latter to form tin tetrachloride or stannic chloride, $SnCl_4$, which distils over as a colourless liquid of density 2·2 and boiling point 120°. It fumes strongly in the air as it undergoes decomposition with water; it dissolves in water with considerable evolution of heat, forming a clear liquid. This still contains, especially when concentrated, a portion of the chloride dissolved unchanged, for on boiling this passes over with the steam. The greatest part is, however, hydrolytically dissociated, and the dilute solution contains essentially hydrochloric acid along with colloidally dissolved stannic hydroxide. This is proved by the fact that the solution exhibits all the properties of a correspondingly dilute solution of hydrochloric acid, and also by the fact that in course of time the greater portion of the tin separates out as a white, gelatinous precipitate of stannic hydroxide.

When small quantities of water are allowed to combine with stannic chloride, rise of temperature being avoided, various hydrates are formed with from three to nine moles of water of crystallisation, the first of which is the most stable. They are crystalline substances which dissolve in water, and yield solutions which exhibit the same properties as the solution of the tetrachloride when prepared directly.

The tetrachloride combines with hydrochloric acid to form a hydrochlorostannic acid, H_2SnCl_6, which can also be obtained in the solid state with $6H_2O$. The crystals melt as low as 28°. The acid forms good crystalline alkali salts, which are also formed from tin tetrachloride and the respective alkali chlorides. The ammonium salt, $(NH_4)_2SnCl_6$, crystallises anhydrous, and is used as a mordant in dyeing under the name of *pink salt.*

Stannic hydroxide, which slowly separates out from the aqueous solution of stannic chloride, is immediately obtained by saturating the solution with a base. A gelatinous precipitate of $Sn(OH)_4$ is formed, which dissolves in dilute acids; from these solutions it again separates spontaneously after some time. We are probably dealing here with a colloidal solution which undergoes decomposition, for the reason that the stannic hydroxide is slowly converted into another less soluble form. The same transformation also occurs in the original hydrochloric acid solution, for the hydroxide precipitated from solutions of different ages has different properties.

The precipitate redissolves in excess of caustic potash or soda, a stannic salt or stannate being formed. The solution has a strongly alkaline reaction, showing that the salt is hydrolytically dissociated. From the solution in caustic potash a salt, K_2SnO_3, can be obtained in crystals; in this case, therefore, the stannic acid is a dibasic acid, comparable with carbonic acid, H_2CO_3. A number of other salts are also known containing several combining weights of tin to two of potassium, and are therefore salts of "condensed" stannic acid; they are, however, as a rule not well characterised, and are unstable.

Differing from this stannic acid there is another compound of like composition, which is obtained by the action of nitric acid on metallic tin, and which is usually called *metastannic acid.* The first action of nitric acid leads to the formation of stannous nitrate, the presence of which can be detected when dilute cold nitric acid is employed. The nitric acid then acts as an oxidising agent on the distannion, and stannic nitrate is formed, which immediately decomposes into stannic hydroxide and free nitric acid. The former separates out, and the separation is complete when the liquid is evaporated to dryness. The hydroxide thus formed has essentially different properties from that obtained from the tetrachloride. It is insoluble in dilute acids; it dissolves, however, when it is warmed with somewhat stronger acids, the acid poured off and replaced by water, although it does not dissolve in the acids themselves. This is due to the fact that it takes up acid and forms salts which, although not soluble in the excess of acid, dissolve in the pure water. It is quickly deposited again from these solutions, especially on the addition of sulphuric acid. Metastannic acid dissolves in alkalis like ordinary stannic acid; from the solution, acids again precipitate metastannic acid. If, however, the salt is fused with excess of caustic potash, other acids precipitate ordinary stannic acid.

The relation of the two stannic acids to one another has not yet been explained. It is probable that there are several intermediate members between the two forms, and that the metastannic acid is the final and most stable form. This is rendered probable from the fact that ordinary stannic acid, when kept for a very long time under water, is converted into a substance with the properties of metastannic acid.

Stannic Sulphide.—From acid solutions of stannic salts, sulphuretted hydrogen precipitates yellow *stannic sulphide*, SnS_2, which is not soluble in dilute acids but is readily soluble in alkali sulphides. Salts of thiostannanion, SnS_3'', many of which have been prepared in the solid state, are thereby formed. From these, acids first of all liberate thiostannic acid, which, however, is just as little stable as the other metallic thio-acids, and decomposes into sulphuretted hydrogen and tin disulphide.

Stannic sulphide can also be obtained in the dry way by heating tin and sulphur (best with addition of ammonium chloride), a crystalline product with a gold lustre being thereby formed, consisting of small scales. On account of its gold-like appearance, it is called *mosaic gold.*

Alloys of Tin.—Tin can be fused in all proportions with most of the other metals, and yields alloys, many of which are applied in the arts. With lead it yields a white alloy which fuses more easily than its components; it is used as a *soft solder* for uniting other metals.

With copper, tin forms alloys which have more the character of chemical compounds, since their properties deviate from those of the components. According to the amount of the tin, there are obtained bronze for statues and guns, bell-metal, and specular metal. Britannia metal (p. 705) consists of tin with $\frac{1}{10}$th part of antimony.

Tin is very largely employed for the purpose of coating other metals. Copper utensils used for cooking purposes are tinned in order to prevent poisonous copper compounds getting into the food. Further, sheet-iron on being tinned is covered with a white layer of almost silver lustre, which prevents the iron from rusting and allows of it being easily united by means of soft solder (*vide supra*). *Tin-plate* made in this way has an extremely wide application; the manufacture of air-tight vessels for preserving provisions (conserve tins) need only be recalled. Iron vessels which have been tinned in the piece are more durable than articles made of tin-plate; in these, unprotected spots produced in the process of manufacture are present, and at these the tin-plate rusts through on contact with water.

Finally, the use of tin for coating glass mirrors may be mentioned. For this purpose a piece of tinfoil of sufficient size is amalgamated, *i.e.* is coated with mercury, and on it is placed a well-cleaned glass plate. By placing the plate upright, the excess of mercury is allowed to run off, and a crystalline amalgam is gradually formed which lies close to the glass of the mirror. At the present day the tin-mercury mirrors have been almost entirely superseded by the silvered ones: on account of the much smaller thickness of the silver layer such mirrors can be made more cheaply than the mercury ones; the manufacture of the latter, moreover, is not free from objection, on account of the poisonous nature of the mercury.

Titanium, Germanium, Zirconium, and Thorium.—These elements are directly allied to tin. With the exception of the first-named, they occur only sparingly in the earth's crust. In respect of their properties they occupy a position between silicon and tin in such a manner that with increasing combining weight the metallic character becomes more and more developed. They are distinguished by the formation of readily volatile tetrachlorides, the boiling point of which, however, rapidly rises with increasing combining weight, and their most important compounds correspond to the tetravalent type. This is the chief reason for classing them with tin. No such reasons would be furnished by the sulphur compounds, because, with the exception of that of germanium, these are so unstable that they cannot be prepared in aqueous solution.

The similarity of the above-named elements to silicon is seen in their power of forming with fluorine a complex anion of the type MF_6'', the salts of which are mostly difficultly soluble and crystallise well.

Titanium.—Compounds of titanium occur, it is true, very widely distributed in nature, but they are nowhere found in large quantities, and they therefore escape direct observation. The occurrence of the element is in the form of titanium dioxide, TiO_2, or its salts.

Titanium dioxide furnishes an excellent example of polymorphism, for it occurs naturally in three different forms, having different crystalline shape, different density, etc. The most frequently occurring is *rutile*, which crystallises in the quadratic system isomorphous with tinstone. *Anatase* is also quadratic, but has quite different properties, and the third rhombic form is called *brookite*.

Titanium dioxide is, like silicon dioxide, the anhydride of a very weak acid; the alkali salts of the latter are obtained by fusing the dioxide with the hydroxides or carbonates of the alkalis. These salts, *e.g.* potassium titanate, K_2TiO_3, are decomposed by water, difficultly soluble acid titanate being deposited and free alkali passing into solution.

On the other hand, titanium dioxide exhibits feebly basic properties, for the above precipitate dissolves in acids to a clear liquid. A like solution is also obtained by dissolving the corresponding titanium tetrachloride (*vide infra*) in water. Apparently, however, the solution is of a colloidal nature, for on being heated for some time, especially in sulphuric acid solution (or in hydrochloric acid solution with addition of sodium sulphate), titanic acid separates out as a precipitate which is now no longer soluble in acids. This process is employed for the separation of titanic acid from its compounds after these have been rendered soluble by fusion with acid potassium sulphate. Titanic acid, therefore, behaves similarly to stannic acid, and the corresponding two modifications have also been observed in its case. In the latter case as in the former, however, we are probably dealing with the end-members of a continuous series of varying states.

By heating titanium dioxide with charcoal in a current of chlorine, *titanium tetrachloride*, $TiCl_4$, is obtained as a liquid boiling at 135°, which fumes strongly in the air and dissolves in water with great rise of temperature, forming a clear liquid. By neutralising this liquid, a precipitate of titanic acid soluble in acids (*vide supra*) is obtained.

While there are no signs of the formation of a hydrochlorotitanic acid, a fluotitananion, TiF_6'', is known. It is very readily formed by the action of hydrofluoric acid on titanic acid. The free acid may be assumed in the solutions thus formed; it is not known in the pure state. Of its salts, the potassium salt, $K_2TiF_6 . H_2O$, is best known; it is a salt which is rather difficultly soluble in water (9 parts in 100 parts water at room temperature), and can be easily obtained in large crystals by dissolving titanic acid in hydrofluoric acid and adding a potassium salt. In these compounds, the similarity to silicon is especially well seen (p. 464).

Besides the tetravalent stage of titanium, there also exist a divalent, a trivalent, and a hexavalent stage, but these are of subordinate importance. By heating the vapour of the tetrachloride with hydrogen, the trichloride is obtained in the form of violet scales, which dissolve in water, yielding a violet liquid which readily oxidises in the air and deposits titanic acid. These violet solutions can also be obtained from the acid solutions of titanic acid by reduction with zinc or sodium amalgam. With hydrofluoric acid and soluble fluorides, salts of a trivalent anion, TiF_6'', are formed, which are also of violet colour.

If titanium trichloride is heated alone, it decomposes into tetrachloride, which escapes, and difficultly volatile dichloride, which collects in the colder parts of the apparatus as a black crystalline mass, volatile at a red-heat. The compound reacts violently with water, and yields a yellow-brown solution which oxidises in the air. Compounds of this series are also obtained by the very energetic reduction of the acid titanic solutions with sodium amalgam.

Finally, there is a still higher stage of oxidation of titanium which is obtained when hydrogen peroxide is added to a solution of titanic acid in concentrated sulphuric acid. The liquid immediately becomes deep yellow in colour, and the reaction is visible with such small quantities that it is employed as one of the best methods of detecting hydrogen peroxide. By neutralising the sulphuric acid, a yellow, solid substance of the composition TiO_3 can be separated.

Titanium Nitride.—Titanium exhibits a special tendency to combine with nitrogen. It unites so readily with the latter at moderately high temperatures that most of the preparations which were formerly regarded as metallic titanium consisted chiefly of titanium nitride. A substance with a metallic lustre, which is frequently found in blast furnaces and was formerly regarded as metallic titanium, has been recognised as titanium cyanide, $Ti_{10}C_2N_8$. If potassium fluorotitanate is reduced with sodium or potassium, the titanium formed at once combines with the nitrogen of the air. Of these nitrogen compounds, which are most easily obtained by heating titanic chloride with ammonia in a red-hot tube, two are known corresponding to the formulæ Ti_3N_4 and TiN_2. These are crystalline substances with a metallic lustre, which evolve ammonia copiously on being fused with caustic potash or soda, passing thereby into titanates.

The combining weight of titanium is Ti = 48·1.

Germanium is an element of extremely rare occurrence. It can be reduced from its oxygen compounds by ignition with charcoal, and is thus obtained as a very brittle metal which fuses at about 900° and has the density of 5·5; it is insoluble in dilute acids, is dissolved by aqua regia, and is converted into the dioxide by nitric acid. It forms a divalent and tetravalent series of compounds; the tetravalent is the more stable.

Germanium dioxide, GeO_2, is formed by heating the metal in air, and is a white powder which, with water, first forms a milky fluid and then passes into solution. It dissolves in alkalis, forming salts of germanic acid, and is also soluble in acids; it behaves, therefore, like tin dioxide. These salt-like compounds are not well characterised.

With chlorine, germanium forms a tetrachloride, $GeCl_4$, which is a colourless liquid fuming in moist air; it boils as low as 86°, and dissolves in water with rise of temperature. The compound $GeHCl_3$, "germanium chloroform" (cf. p. 400), is formed by the action of hydrogen chloride on metallic germanium; it is very similar to the tetrachloride, and boils at 72°.

Germanium fluoride is not known; a hydrofluogermanic acid, H_2GeF_6, however, exists, which has a similar composition to hydrofluosilicic acid, and forms well-crystallised salts, most of which are difficultly soluble in water.

Germanium sulphide, GeS_2, is a white powder which very readily passes into the colloidal condition, and can therefore be precipitated only by a large excess of acids. It is formed when salts of thiogerman-anion, GeS_3'', produced by the addition of soluble sulphides to solutions containing germanium, are decomposed by excess of acid. It is somewhat soluble in water, and gives coloured precipitates with metallic salts. The mineral *argyrodite* is a silver salt of thiogermanic acid, and in it germanium was first discovered by Winkler in 1886.

Of the compounds belonging to the divalent series, germanous sulphide is the best known; it is obtained by the careful reduction of germanic sulphide, and forms grey-black clusters with a metallic lustre. From aqueous solutions it is deposited as a red-brown precipitate insoluble in excess of acids. Towards alkali sulphides it behaves like stannous sulphide. It is slightly soluble in water.

Zirconium has received its name from the mineral zircon, a silicate of zirconia; the latter was recognised as a distinct earth by Klaproth in 1789. Metallic zirconium is obtained by heating the potassium fluoro-compound with aluminium or sodium; with the former, under suitable conditions (high temperature), a very difficultly fusible crystalline zirconium is obtained in bright grey laminæ; with the latter, a black powder of amorphous zirconium, which readily passes into colloidal suspension, is obtained. The crystalline form is very resistant to chemical attack, and passes into combination only at high temperatures. The combining weight is $Zr = 90{\cdot}7$.

Zirconium forms only one series of compounds, belonging to the tetravalent type. The hydroxide has essentially a basic character. since it does not dissolve in alkalis; its properties are, however, those of a very feeble base. It is obtained by bringing zirconium into solution by fusion with acid sodium sulphate and precipitating the zirconia with ammonia. After drying, the precipitate has the composition $ZrO(OH)_2$, and is slightly soluble in water; the solution reacts alkaline. Even on standing under the liquid in the heat it passes into a difficultly soluble form; on heating the dried substance, it suddenly becomes incandescent, the anhydride being formed; the latter is not soluble in dilute acids, and can be brought into solution only by long heating with concentrated sulphuric acid.

The normal zirconium salts are derived from the tetravalent hydroxide $Zr(OH)_4$; of these the sulphate $Zr(SO_4)_2$ is the best known. It is obtained as a readily soluble, crystalline mass containing $4H_2O$, which on being heated loses water and swells up like alum. The hot solution of the sulphate dissolves a further quantity of the hydroxide and forms basic salts; acid salts are also known.

The naturally occurring mineral zircon is the normal silicate, $ZrSiO_4$. The red-coloured varieties are called jacinth, and are used as gems.

On heating a mixture of zirconium dioxide and charcoal in a current of chlorine, zirconium tetrachloride, $ZrCl_4$, is formed as a white, fairly readily volatile mass.

The corresponding zirconium tetrafluoride is a white, much more difficultly volatile substance, which forms hydrofluorozirconic acid, H_2ZrF_6, with hydrofluoric acid; the salts of the latter are difficultly soluble, and mostly crystallise well. Besides the salts of this type, others have been prepared which can be regarded as double salts with the alkali fluorides.

A zirconium sulphide cannot be prepared in the wet way; it can be obtained from the elements by heating.

Thorium.—This element forms the last member of the tin group, and has, at the same time, one of the highest combining weights. It was discovered by Berzelius in 1828 after he had previously, and erroneously, regarded yttrium phosphate as a new earth, and had called it thoria. Its combining weight is Th = 232·5.

Like zirconium, thorium chiefly occurs as the silicate, *thorite*, and also as a constituent of various rare minerals. While for a long time it was regarded merely as a chemical rarity, it has attained in recent times to a position of great technical importance, since the luminous mass of the incandescent light, the incandescent "mantle," consists essentially of thoria.

Metallic thorium is obtained from potassium fluorothorate by reduction with potassium. It is a grey powder with a metallic lustre, which has hitherto never been fused, and which burns in oxygen at moderately high temperatures with a brilliant light.

In its compounds, thorium appears as tetravalent; its hydroxide, although no strong base, still exhibits the basic properties developed to a higher degree than in the case of the allied substances of lower combining weight. It is precipitated from its salts by ammonia or alkalis, and is not soluble in excess of the precipitant. Similarly to the other dioxides of this group it occurs in several forms possessing different degrees of stability; while the freshly prepared, white, gelatinous hydroxide readily dissolves in acids, a difficultly soluble modification is formed on heating. On ignition, the hydroxide passes into the dioxide, ThO_2, which is a white, light powder. This oxide is not soluble in acids except in hot, concentrated sulphuric acid. The oxide obtained by heating the oxalate, on being evaporated with nitric acid or hydrochoric acid, gives a residue which does not dissolve in dilute acid but is soluble in water; the solution is of a colloidal character. This behaviour recalls that of stannic acid (p. 724).

Of the salts, the sulphate and the nitrate are the best known. *Thorium sulphate*, $Th(SO_4)_2$, crystallises according to the temperature with varying amounts of water. These different forms change comparatively slowly into one another, so that it is easy to prepare solutions of one of these forms which are greatly supersaturated for the other forms. To this is due a peculiar behaviour of the sulphate, which is made use of for the purification of the thorium compounds. The anhydrous sulphate, prepared by heating, is dissolved in ice-cold water. A solution is thus produced which is saturated in respect of the anhydrous salt, but greatly supersaturated in respect of a hydrated salt with $4H_2O$. Since, also, the solubility of this latter salt decreases greatly with rising temperature, a solution prepared in the cold with the anhydrous salt will become, on heating, more and more supersaturated in respect of the salt with $4H_2O$, and the spontaneous separation of this hydrate therefore soon occurs. On heating the salt which is deposited until it has lost its water of crystallisation it again becomes readily soluble in cold water, and behaves as above described.

Thorium nitrate, $Th(NO_3)_4 . 6H_2O$, is a very readily soluble salt, which is obtained by dissolving freshly precipitated thoria in nitric acid. It is used for the preparation of incandescent mantles, a cotton web being moistened with this salt, dried, and heated. The texture burns and the thoria remains as a white, coherent frame-work. By ignition in a Bunsen flame produced under pressure, whereby the material appreciably contracts, the mantles are made ready for use.

The mantles are rendered luminous by being strongly heated in a specially constructed Bunsen flame. It is a remarkable fact that pure thoria gives only a poorly luminous mantle; in order that it may become powerfully luminous small quantities of certain other substances must be added. For this purpose the addition of 1 per cent of cerium oxide (p. 560) has been found to be best. The cause of this influence has not yet been established quite free from doubt, but the most probable view is that the addition effects a catalytic acceleration of the combustion of the mixture of coal-gas and air in direct contact with the skeleton of thoria, whereby a correspondingly higher temperature is produced.

The tendency to the formation of complex fluorine salts (cf. p. 726) is greatly diminished in the case of thorium; thorium fluoride is a precipitate which does not dissolve in excess of hydrofluoric acid, and does not therefore exhibit the formation of a hydrofluothoric acid. A potassium fluorothorate, $K_2ThF_6 . 4H_2O$, however, is known as an almost insoluble crystalline powder.

A very remarkable property of the thorium compounds is, that influences are emitted by them which penetrate through solid substances and are characterised by their action on the photographic plate as well as by the change in the electrical properties of the air. We shall enter into these points in greater detail when we come to discuss uranium, which exhibits these actions in a much higher degree.

CHAPTER XLII

URANIUM, TUNGSTEN, AND MOLYBDENUM

General.—These three elements resemble chromium in many of their properties, so that they might have been treated in connection with it. On account, however, of their forming thio-acids they so undoubtedly belong to the present class of metals (chromium forms no sulphur compound at all in aqueous solution), that it appears appropriate to separate them from chromium.

The elements uranium, tungsten, and molybdenum are characterised by the fact that their most stable oxygen compounds have the composition MO_3 and are the anhydrides of acids. In accordance with the general rule, the acid properties are least pronounced in the case of the element with the highest combining weight, and become more pronounced as the combining weight decreases.

All three belong to the less frequent elements, although they cannot be characterised as rare. They are difficultly fusible metals, which keep well in the air, but which have found no application in the pure state.

Of all the known elements, uranium has the highest combining weight, viz. $U = 239 \cdot 5$.

Uranium.—Uranium was discovered by Klaproth. In the case of metallic uranium the same thing happened as in the case of vanadium, viz., the copper-brown coloured dioxide which is readily formed by the reduction of the higher oxygen compounds, was mistaken for the metal. The true uranium was subsequently obtained by the action of sodium on the chlorine compound; it is a white, difficultly fusible metal, which dissolves fairly readily in dilute acids, and in the potential series stands near cadmium.

Uranium forms a whole series of stages of combination in which it is trivalent to octavalent. The better known and more important compounds are those of the tetravalent, and especially of the hexavalent type.

By oxidation of the naturally occurring compounds of uranium, salts of uranyl, *i.e.* of the divalent cation $UO_2^{\cdot\cdot}$, are obtained. The normal hydroxide of hexavalent uranium, $U(OH)_6$, has both acid and basic properties. The latter are not sufficiently strongly developed for all the six hydroxyls to be replaceable by acid residues; two, however, can be replaced. In the salts, therefore, there exists the divalent cation $U(OH)_4^{\cdot\cdot}$, or its anhydride $UO_2^{\cdot\cdot}$, uranyl, which forms salts like any other divalent cation.

* This occurrence of an "oxygenated metal" has been regarded as something remarkable and extraordinary, but it is readily intelligible when regarded from the point of view that in polyvalent acids and bases, the replacement of hydrion or hydroxidion becomes more difficult the further the replacement proceeds. Just as in aqueous solution phosphoric acid behaves chiefly as a dibasic acid and forms salts of the anion PO_4H'', since those of the anion PO_4''' suffer too great hydrolysis to be present in any considerable quantity, so the hydrolysis of the uranium salts corresponding to the higher cations $U(OH)_3^{\cdot\cdot\cdot}$, $U(OH)_2^{\cdot\cdot\cdot\cdot}$, etc., is too great for these salts to be present in appreciable amount. For even the second cation, $U(OH)_4^{\cdot\cdot}$, is so greatly hydrolysed that its salts have a distinctly acid reaction.

Diuranylion, $UO_2^{\cdot\cdot}$, is of a bright yellow colour with green fluorescence, and in the spectroscope exhibits a number of definite absorption bands. Of the salts, the nitrate $UO_2(NO_3)_2 . 6H_2O$ is the best known; it forms yellow crystals with green fluorescence, which are readily soluble in water and serve as the starting-point in the preparation of other uranium compounds.

From the nitrate, soluble bases precipitate a yellow substance which consists essentially of uranyl hydroxide, $UO_2(OH)_2$ or $U(OH)_6$, but also always contains a quantity of the base in the form of a uranate or salt of uranic acid (*vide infra*). By evaporating a solution of uranyl nitrate in alcohol (in which the alcohol serves to destroy the nitranion) a yellow powder of the composition $UO_2(OH)_2$, free from alkali, is obtained. With other methods of preparation the composition is $U(OH)_6$. This uranyl hydroxide dissolves in acids and forms the corresponding, often complex, uranyl salts.

Uranyl has a pronounced tendency to form complex compounds; these are formed with almost all organic acids. Of these the oxalate, which is very sensitive to light, and in sunlight evolves gas copiously, is of interest. In this process we do not have an oxidation of the oxalic acid with reduction of the uranyl, but the escaping gas is a mixture of carbon monoxide and carbon dioxide, and a precipitate of uranyl hydroxide is formed at the same time. The oxalic acid therefore undergoes the same decomposition as by heating with elimination of water (p. 410), and the uranium acts catalytically. The uranyl salts of other organic acids exhibit similar decomposition in the light.

With phosphoric acid uranyl forms a phosphate, UO_2HPO_4, insoluble in acetic acid, or, in the presence of ammonium salts, the compound $UO_2(NH_4)PO_4$. This precipitation is used for the volumetric determination of phosphoric acid; for this purpose, ammonium acetat and acetic acid are added to the liquid containing phosphoric acid, an uranyl nitrate solution of known titre is then run in until a drop o the solution gives a red coloration with potassium ferrocyanide. The coloration is due to uranyl ferrocyanide, which is of an intens brown-red colour, and is insoluble in dilute acids.

Uranyl hydroxide can also act as an acid, and forms salts of th type of chromic and dichromic acids. The former are obtained a yellow-red, crystalline masses, not appreciably soluble in water, bu soluble in acids, by igniting uranium compounds with alkali salts i the air. The latter are precipitated from the solutions of the urany salts by the addition of excess of alkali. The precipitates are no soluble in excess of the precipitant. Of these compounds, the sodiun salt, $Na_2U_2O_7 . 6H_2O$, can be obtained commercially under the nam *uranium yellow*, and is used for colouring glass.

Uranium glass is of a bright yellow colour and exhibits a brillian green fluorescence; it is therefore employed for the manufacture o wine-glasses and such articles.

By means of reducing agents, *e.g.* zinc in acid solution, the urany salts are converted into the salts of the tetravalent *uranous* series The solutions thereby become of a fine green colour, which is th colour of tetrauranion, $U^{\cdot\cdot\cdot\cdot}$. The best known of these salts i the sulphate, which is obtained in dark green hydrated crystals $U(SO_4)_2 . 4H_2O$, by exposing a mixture of uranyl sulphate with sul- phuric acid and alcohol to sunlight; the alcohol effects the reductio of the uranyl to the uranous compound. The salt is isomorphou with thorium sulphate (p. 730).

From the solutions, alkalis give a bright green precipitate o uranous hydroxide, $U(OH)_4$, which absorbs oxygen from the air, thereby becoming first brown and then yellow. The anhydride, uranium dioxide, is obtained by igniting uranium compounds in a current o hydrogen; at higher temperatures it forms a copper red mass with a metallic lustre (p. 732).

The naturally occurring *pitchblende* consists essentially of uranou uranate, *i.e.* the uranate of tetravalent uranium, $U(UO_4)_2$, equal t U_3O_8. It is a black mineral which is the source from which the othe uranium compounds are manufactured. This compound is also formed when any oxide of uranium is heated in the air.

Chlorides of Uranium.—As in the case of vanadium, no chloride is known corresponding to the highest stage of combination, but only a pentachloride, which is obtained along with the tetrachloride by igniting uranium oxide with charcoal in a current of chlorine. The two can be separated by means of their different volatility, the compound containing most chlorine being in this case, as always, the more volatile. Uranium pentachloride, UCl_5, is a brown, crystalline substance, which is extremely soluble in water, and readily decomposes into free chlorine and tetrachloride. The latter forms dark-green crystals, which dissolve in water to form a dark-green solution; regarding the latter, it has been stated that it is not of itself oxidised by the atmospheric oxygen, but is so in presence of iron salts. This is apparently another case of catalytic acceleration.

From the tetrachloride, a trichloride, UCl_3, can be obtained by reduction with hydrogen ; this is a brown-red mass which readily dissolves in water, but with the latter forthwith evolves hydrogen and passes into a basic salt of tetravalent uranium. The fresh solution gives with caustic potash a brown precipitate of uranium trihydroxide, which also very quickly oxidises with evolution of hydrogen.

Sulphur Compounds.—Ammonium sulphide deposits a brown precipitate from uranyl salts ; the precipitate is uranyl sulphide, UO_2S, which is, however, partially decomposed. For from the sulphur compound even water splits off sulphuretted hydrogen, which partially reduces the uranic oxide formed, and is converted into sulphur.

Uranium Rays.—In the case of uranium, a property was first observed which, however, has been found to be more a property of pitchblende than of the element uranium ; it consists in the following. If any uranium compound is placed on a photographic plate covered with black paper, the plate undergoes a change as if light had acted on it, *i.e.* it can be developed (p. 678). This action takes place also through thin plates of mica or of glass, but not through thick metal plates.

A further influence emitted by uranium and its compounds is that they make the air electrically conductive. In a space in which the air has been subjected to this influence, an otherwise well insulated electrometer loses its charge.

Finally, certain phosphorescent substances, *e.g.* barium platinocyanide (*vide infra*), are rendered luminous by this action. For this purpose, however, the property must be highly developed, and this is found only in a few cases.

Since all these influences emanate from the substances under such conditions as to make it impossible for them to be due to the emission of ordinary material constituents (such as vapour), they have been designated as a *radiation*, and one speaks therefore of *uranium rays*. This is, however, only an imperfect expression of the case, since some important properties of the phenomena of radiation are wanting.

That these "radiations" have a chemical connection with the uranium is also not probable. From the pitchblendes, other substances have been obtained which have the essential properties of the barium and of the bismuth compounds, and which possess the new property in a very high degree. But here also the property is present in so varying intensity that the impression is produced that the carrier of it is not the particular substance itself, but a substance which is associated with it in varying amounts, and which has not yet been isolated in the pure state. The names radium and polonium, which have been given to these substances, cannot therefore as yet claim to denote definite chemical elements.

The above influences can be so characterised that energy is emitted from the substances named, and can be converted at suitable points into other forms, chemical or optical, and perhaps also electrical, and which in its course is able to pass through partitions which are impermeable for substances in the ordinary sense. The apparent inexhaustibility of these sources of energy could be attributed to the amounts of energy emitted being very small, so that an appreciable diminution of the total store need not occur; on the other hand, however, indications of such diminution have indeed been observed in the case of the more active preparations.

Whether in these processes energy is alone transmitted, or whether a migration of matter accompanies the migration of energy, can also as yet not be decided. So much only is certain that if a migration of ponderable matter does occur, it concerns much smaller quantities than it has hitherto been customary to measure.

Tungsten.—This element was discovered in 1781 by Scheele. Metallic tungsten can be obtained by the reduction of its oxide in a current of hydrogen or with charcoal; it is a grey, very difficultly fusible, hard metal, the density of which is 16. On account of these two properties it would be very suitable for cannon balls if its difficult fusibility did not act as a hindrance to its manipulation. It finds technical application as an addition to steel (tungsten steel).

The combining weight is W = 184.

Tungsten forms many compounds in which it appears as divalent to hexavalent. The lower stages have basic properties; the highest oxygen compound is a pronounced acid anhydride. Of all the stages, it is the most stable.

Tungsten trioxide, WO_3, the anhydride of tungstic acid, is obtained as a yellow powder by the action of acids on its salts, some of which occur naturally; it is very slightly soluble in water, but readily dissolves in alkalis. According to the temperature of precipitation, there is obtained the anhydride (in the heat) or the hydroxides $WO(OH)_4$ and $WO_2(OH)_2$.

By dissolving the oxide or hydroxide in the calculated amount of caustic potash or caustic soda solution, and evaporating to the point of crystallisation, the normal tungstates K_2WO_4 and Na_2WO_4 are obtained in hydrated crystals. These pass, however, with extreme ease into salts of more complex composition, the tungstic acid forming condensed acids, which partly crystallise out with the normal tungstates as double salts.

Normal tungstates occur in nature, and constitute the ores of tungsten. The ferrous compound, $FeWO_4$, is called *wolfram;* the calcium compound, $CaWO_4$, *scheelite;* the lead salt, *scheeletine.*

On boiling a solution of an alkali tungstate with excess of trioxide, large quantities of the latter are dissolved, and the *metatungstates*, $M_2W_4O_{13}$, are formed in which a very stable condensed tungstanion, W_4O_{13}'', is present, the reactions of which differ entirely from those of ordinary tungstanion, WO_4''. For example, the dissolved salts are not precipitated by acids. By the action of sulphuric acid on the difficultly soluble barium salt, a solution of metatungstic acid can be obtained, from which the latter can be obtained in yellow, extremely soluble crystals, by evaporation.

Different from metatungstic acid, there is the so-called colloidal tungstic acid, which is obtained by dialysing a solution of a normal tungstate slightly acidified with hydrochloric acid. The liquid dries up to a gummy mass, which re-dissolves in water, forming a sticky liquid; it does not taste acid, and is not precipitated from solution by salts or other substances, as happens in the case of colloids. The solution also exhibits an appreciable depression of the freezing point which leads to the (doubtful) formula $H_2W_3O_{10}$.

Besides the above, other diversities have also been observed in the case of tungstic acid, depending on the very ready and often occurring formation of complex acids with other acids. The compounds with silicic acid have been most thoroughly investigated; similar compounds with phosphoric, arsenic, vanadic, iodic, boric, and other acids also exist. The composition is that of the above acids plus a definite, generally a larger number of combining weights of WO_3; in the process, the basicity of the other acids generally remains unchanged, but the complex acids produced are mostly considerably stronger than the mother substances. A description of the different compounds would take us too far.

On treating tungstates with zinc in acid solution, the liquid becomes dark blue, and on further reduction brown. It then contains the tetravalent ion $W^{\cdot\cdot\cdot\cdot}$. From this, tungstic acid is again readily formed by means of oxidising agents.

Very varied compounds of the general formula $Na_m(WO_3)_n$ are obtained by weak reduction of sodium tungstate (by fusion with tin); these have all a fine metallic lustre, have different colour according to the amount of tungsten they contain, conduct electricity like a metal, and are extremely resistant to the action of water, acids, and bases. They find an application as "tungsten bronze."

Chlorides of Tungsten.—On heating metallic tungsten in a current of chlorine, with careful exclusion of oxygen, the hexachloride, WCl_6, s obtained in black-violet crystals, which melt at 275° and boil at 347°. The vapour contains a little free chlorine, so that on repeated distillation chlorine escapes, and the lower stage, tungsten pentachloride, WCl_5, is formed in black green crystalline needles, which melt at 248° and boil at 276°. This substance also readily splits off chlorine, and on distillation in a current of an indifferent gas leaves a residue of tungsten tetrachloride, WCl_4, as a non-volatile, grey-brown mass. By the action of reducing agents, *e.g.* of hydrogen, this compound finally passes into the dichloride, WCl_2, which has a similar appearance.

Besides these compounds, the oxychlorides, viz. $WOCl_4$ and WO_2Cl_2, are very readily formed in the presence of oxygen or water. The first compound forms long, dark red needles, melting at 210° and boiling at 228°; the second, which is comparable with chromyl chloride, appears in bright yellow laminæ, the melting point of which lies above the temperature of sublimation (about 270°). On distillation it readily decomposes into the preceding compound and a residue of tungsten trioxide. Both undergo violent decomposition with water, forming tungstic acid and hydrogen chloride.

Sulphur Compounds.—The acid-forming properties of tungsten are exhibited also by its sulphur compounds, for it forms thiotungstates in which the oxygen of the tungstates is gradually replaced by sulphur.

By passing sulphuretted hydrogen into a solution of an alkali tungstate, the corresponding thiotungstate, M_2WS_4, is obtained only when there is excess of alkali hydrosulphide. If no excess is present, on dilution with water the sulphur in the thio-acid is gradually replaced by oxygen, sulphuretted hydrogen being evolved. Thiotungstanion is yellow in colour; by replacing the sulphur with oxygen, the colour becomes correspondingly paler.

On adding acids to the thiotungstates, tungsten sulphide is precipitated, and sulphuretted hydrogen is evolved, thiotungstic acid, which is primarily formed, decomposing as usual into these components. Tungsten trisulphide is thus obtained as a brown, amorphous precipitate which passes into colloidal solution in water.

From tungsten and sulphur at a high temperature, a lower sulphide, WS_2, is obtained in grey, graphite-like laminæ, which are very stable.

Molybdenum.—The chemical individuality of molybdenum, like that of tungsten, was established by Scheele, although the metal was not obtained till later.

Molybdenum resembles the related elements in respect of the variety of its compounds, for its valency varies from two to six. In this case also, the compounds of the hexavalent type are the most stable.

The combining weight of molybdenum is 96·0.

Metallic molybdenum is obtained as a white, very difficultly fusible metal which, like iron, becomes more readily fusible and very hard through absorption of carbon. It is not attacked by dilute acids and is oxidised by nitric acid. In the potential series, it appears to stand in the neighbourhood of lead.

Molybdenum Trioxide, the anhydride of molybdic acid, is obtained in the crude state by roasting the naturally occurring molybdenum sulphide, and is purified by dissolving in ammonia and repeated roasting. It is a white substance which becomes yellow on heating: at a red heat it melts and volatilises. It is readily reduced to the metal by means of hydrogen and charcoal.

Molybdenum trioxide is the anhydride of a series of acids which are formed from it and the elements of water in varying proportions. Whereas in the case of tungstic acid the metatungstic acid at least was found to be well characterised and stable, no similar compound is known in the present case, but the different polymolybdic acids appear to pass quickly and readily into one another. Compounds of trimolybdic acid, $H_2Mo_3O_{10}$, are the most frequent.

The power of forming complex acids is here developed to a particularly high degree, and molybdenum trioxide appears to unite with practically all other acids to form such compounds. For while pure molybdenum trioxide, or its hydrate, is only sparingly soluble in water, it passes abundantly into solution in free acids; salts of molybdic acid therefore give no precipitate of molybdic acid on adding excess of another acid.

Of these complex compounds the phosphomolybdic acid $H_3PO_4 . 10MoO_3$ is the best known. Besides the compound with $10MoO_3$ there are also compounds with perfectly similar properties containing $11MoO_3$ and $12MoO_3$.

The very difficultly soluble ammonium salt of these acids is obtained by warming an acid solution of ammonium molybdate with a liquid containing phosphoric acid. The liquid first becomes yellow and then deposits a yellow powder, which is the above ammonium salt. As is frequently the case in the formation of complex compounds, the reaction does not take place instantaneously, but requires a moderately long time for its completion.

* Since the reaction occurs in acid solution, and since a very large quantity of precipitate is obtained for a small quantity of phosphoric acid, the reaction is employed for the detection of phosphoric acid in analysis. Care must be taken that the molybdic acid is present in excess as, otherwise, soluble compounds can be formed.

From the ammonium salt the free phosphomolybdic acid can be obtained by warming with aqua regia, whereby the ammonia is destroyed with evolution of nitrogen. The solution on concentration yields fine crystals of the free acid. It can also be obtained by warming phosphoric acid and molybdic acid in the requisite proportions. Pyro- and meta-phosphoric acids do not give these compounds. This free acid is yellow, very readily soluble in water, and yields precipitates with the organic "alkaloids" (basic derivatives of ammonia which occur in plants and have mostly a powerful physioogical action); it serves therefore as a reagent for these.

Lower Oxygen Compounds.—If zinc is introduced into the acid solution of molybdic acid, the liquid first becomes blue, and on further reduction passes through various colours into brown. The solution then contains a salt of the sesquioxide, Mo_2O_3. By very powerful reduction one can descend still lower; the resulting solution, however, oxidises with extreme readiness.

From molybdenum trioxide, the sesquioxide, Mo_2O_3, is obtained as a black powder by reduction with hydrogen at a red heat. If the temperature is only moderately high, the dioxide MoO_2 is obtained as a crystalline, violet, or copper-coloured mass. Between this and the trioxide are the readily formed blue compounds, the composition of which varies and cannot be characterised with sufficient sharpness.

Chlorine Compounds of Molybdenum.—A chloride corresponding to molybdenum trioxide is not known; the highest chlorine stage is a pentachloride, $MoCl_5$. This is obtained by gently warming metallic molybdenum in a current of chlorine; it is a dark red vapour, which condenses to a liquid, boiling at 268° and solidifying at 194° to dark green crystals. The chloride reacts violently with water and yields a blue liquid which deposits a brown precipitate of molybdenum tetrahydroxide on addition of alkalis, while a molybdate remains in solution.

When the pentachloride is carefully heated in a current of hydrogen, it passes into molybdenum trichloride, which is very similar in appearance to red phosphorus. On being more strongly heated, this decomposes into difficultly volatile dichloride, which remains behind, and tetrachloride which volatilises. The former is a yellow, non-crystalline mass, the latter a brown powder. All the chlorides react energetically and undergo double decomposition with water.

Besides the chlorides, there are also a number of oxychlorides, some of which are very readily formed. The compound MoO_2Cl_2 is yellow-white in colour, and is obtained by heating a mixture of molybdenum trioxide and charcoal in a current of chlorine. Besides it there are also formed the violet compound $Mo_2O_3Cl_6$, and the green $MoOCl_4$, which become more volatile as the amount of chlorine increases; the compound last mentioned volatilises even under 100°.

Molybdenum trioxide volatilises very readily at 150°-200° in a current of chlorine; this is due to the formation of a compound: $H_2MoO_3Cl_2 = MoO_3 + 2HCl$. Salts of molybdic acid are also decomposed, the molybdic acid escaping and a chloride of the particular metal remaining behind.

Sulphur Compounds.—In nature the compound MoS_2 occurs as molybdenum glance. It is a grey-black substance, similar to graphite, and is the source from which the other molybdenum compounds are obtained.

On passing sulphuretted hydrogen into the solutions of the alkali molybdates, the liquid becomes intense red-brown in colour and contains a corresponding *thiomolybdate*. A similar variety to that shown by the salts of molybdic acid is found also in the case of the salts of thiomolybdic acid, with respect of the relation between acid and base, so that the description of the different compounds would lead too far. On adding an acid to the solutions, a precipitate of molybdenum trisulphide is formed with evolution of sulphuretted hydrogen; it is a red-brown substance, which gives a colloidal solution with pure water.

CHAPTER XLIII

GOLD AND THE PLATINUM METALS

General.—The metals which have to be treated in this chapter constitute, along with silver, the group of the noble metals. By this designation there is understood metals which do not unite with the oxygen of the air either at high or low temperatures, and which can be converted only with difficulty into compounds by means of chemical reactions. In other words, they are metallic elements which in the elementary state contain much less free energy than their compounds.

Such a statement cannot of course be made quite general, since it depends on the nature of the compounds what difference of energy exists between their free energy and that of their components. Thus, in fact, we see that towards certain reagents the noble metals behave as base, *i.e.* pass spontaneously into compounds. The reagents which have this action on the noble metals are chiefly those by which the metals are converted into complex compounds.

Of the elements grouped together in this chapter, gold occupies a rather solitary position, while the six platinum metals form a well-arranged group of three pairs. This is seen from the following table, in which the neighbouring elements are especially similar to one another. The chemical similarity follows the values of the combining weights :—

Palladium . . .	106	Platinum . .	194·8
Rhodium . . .	103·0	Iridium . . .	193·0
Ruthenium . .	101·7	Osmium . . .	191

Gold.—The element gold occurs in nature almost entirely in the metallic state ; in spite of its rarity it may, by reason of its remarkable properties, be regarded as that element which has been longest known and which was earliest used.

Gold is a lustrous, yellow metal, whose density is 19·3, and which melts at 1035°. In the air, it remains unchanged at all temperatures ; moisture also has no influence on its lustre. By reason of its unalterability it has been used from olden times as a standard of value and for enabling this standard to be preserved. At the present day it has been adopted by most countries as the basis of their coinage.

Gold is not attacked by dilute or concentrated acids, so that it remains as a residue (as a brown powder) when auriferous metal is treated with nitric acid or with concentrated sulphuric acid, which has a similar action. On the other hand, it dissolves fairly readily in chlorine water and in other liquids which give off free chlorine. A mixture of nitric and hydrochloric acids has the latter property (p. 334), and is used under the name of "aqua regia" (since it dissolves the king of the metals) for the preparation of gold compounds.

Of the mechanical properties of gold its malleability is the chief; this allows of the metal being rolled or beaten out to extremely thin leaves. These leaves transmit green light. Still thinner films of gold are obtained by chemical precipitation from solution. Finely divided gold, such as is obtained by reduction on the skin when this is moistened with gold solution, appears red-violet. This property is made use of in photography for the purpose of imparting the well-known brown-violet "photographic tint" to the brown positives, consisting of finely divided silver (p. 677). For this purpose the pictures are treated with a very dilute, neutral or alkaline solution of gold, whereby the gold is precipitated by the metallic silver of the picture, while the silver passes into the corresponding compound.

Gold which is precipated from solution in a very finely divided condition, generally appears blue by transmitted light, while the incident light is dispersed with a brown colour. If, however, precipitation takes place in a very diluted condition, purple-red solutions of colloidal gold are obtained; these are precipitated by salts and exhibit the general properties of colloidal solutions.

* The simplest means of obtaining such solutions consists in allowing an electric arc to pass between electrodes of gold under water to which a trace of alkali has been added.

In fused glass also, gold dissolves in a colloidal condition and yields the fine red-coloured gold-ruby glass. Finally, a solid solution of colloidal gold in stannic acid, obtained by the precipitation of gold solutions with stannous chloride, has long been known by the name of purple of Cassius, and is employed in porcelain painting.

The combining weight of gold is Au = 197·2.

Gold Compounds.—Regarding the ions formed by gold there is as yet no sufficient knowledge. It is known that gold acts both as a mono- and as a tri-valent element; in the solutions also of the trivalent compounds, trivalent triaurion, $Au^{\cdot\cdot\cdot}$, can be assumed (the monovalent gold compounds are not appreciably soluble in water); it is, however, unknown in what proportion these solutions contain the ion $Au^{\cdot\cdot\cdot}$ along with other, complex ions, such as gold forms with ease and in considerable numbers.

The best known gold compound is gold chloride, which is formed on dissolving gold in aqua regia. A yellow solution is produced from which hydrochloroauric acid, $HAuCl_4$, can be obtained in yellow, readily soluble crystals, by careful evaporation. On heating somewhat more strongly, hydrogen chloride escapes and gold trichloride, $AuCl_3$, remains behind as a brown, crystalline mass which is also readily soluble. Its aqueous solution has an acid reaction and contains the gold in the form of a complex anion of the composition $AuOCl_3''$, for the trichloride unites with the solvent water to form the compound H_2AuOCl_3, which partially dissociates into its ions. By no means all the gold chloride, however, appears to undergo this transformation.

The hydrochloroauric acid, $HAuCl_4$, is much better characterised. A large number of well-crystallised salts of this are known which, however, are generally designated as "gold chloride double salts." They are obtained by the action of the solution of hydrochloroauric acid on any salts of the particular base, best on the chlorides; they are often used for the characterisation of organic bases.

Of the salts of chloroauranion, $AuCl_4'$, the potassium salt has to be mentioned which, according to the conditions of crystallisation, crystallises with varying amounts of water (over sulphuric acid in anhydrous crystals); also the sodium salt $NaAuCl_4 . 2H_2O$, which is employed as "gold salt" in photography (p. 743).

Strong bases decompose both the trichloride and the hydrochloroauric acid, and a yellow-brown precipitate of (impure) auric hydroxide, $Au(OH)_3$, is formed; this is soluble in excess of the base, since the hydroxide has weak acid properties. The potassium aurate, $KAuO_2$, which is formed under these conditions has also been obtained in the solid state as a bright coloured salt, from which metallic gold is very readily precipitated (*e.g.* by dust).

By precipitating gold chloride with baryta, difficultly soluble barium aurate is obtained which leaves a residue of fairly pure gold hydroxide on being treated with dilute nitric acid. This hydroxide does not dissolve in dilute acids but does so in concentrated nitric acid, with which it forms a nitroauric acid similar to hydrochloroauric acid. Gold trihydroxide must therefore be regarded as an essentially acid hydroxide.

From solutions of gold, reducing agents of all kinds, *e.g.* ferrous salts, sulphurous acid, oxalic acid, etc., precipitate metallic gold, which according to the conditions of experiment, appears as a yellow precipitate of metallic lustre or as a brown powder. The commencement of the separation is always signalised by the solutions assuming a blue coloration by transmitted light.

Aurous Chloride.—By carefully heating gold chloride to 180°, the compound AuCl is obtained according to the equation: $AuCl_3 = AuCl + Cl_2$. It is a yellow-white powder, which does not dissolve in water but decomposes according to the equation,

$3AuCl = AuCl_3 + 2Au$, into gold trichloride which dissolves, and metallic gold, which remains behind. Aurous chloride forms with the alkali chlorides complex salts, which can be derived from a chloroaurosion, $AuCl_2'$. They are obtained by carefully heating the corresponding auric compounds; on dissolution in water, however, these salts undergo the same decomposition as aurous chloride.

Sulphur Compounds.—On account of the reducing action of sulphuretted hydrogen, the sulphur compounds of the aurous series are more stable and more easily prepared than those of the auric series. Aurous sulphide, Au_2S, is obtained (mixed with sulphur) by passing sulphuretted hydrogen into a boiling solution of gold chloride. It is a dark precipitate which yields a brown colloidal solution with pure water. The solution does not exhibit the reactions of a sulphide, and therefore contains only a negligible amount of ions.

Aurous sulphide unites with alkali sulphides to form thio-salts of the formula MAuS, which are soluble in water but are quickly decomposed in the air owing to oxidation. By fusion with alkali sulphides, therefore, gold is rendered soluble owing to the formation of the above compounds. They are immediately decomposed by acids

On treating a solution of gold chloride in the cold with sulphuretted hydrogen, a more highly sulphuretted compound of gold, having approximately the composition AuS or Au_2S_2, is precipitated. It is a black amorphous mass which decomposes into gold and sulphur on being heated, is insoluble in acids, and can be brought into colloidal solution by treating with potassium cyanide and then with pure water. This precipitate dissolves in yellow but not in colourless ammonium sulphide, with formation of ammonium thioaurate, NH_4AuS_2.

Complex Gold Compounds.—As is evident from the description of the more simple gold compounds, the saline derivatives of gold are chiefly of a complex character, *i.e.* the gold is not present in them as an elementary ion. Besides these there also exist a large number of other complex gold compounds; such compounds are formed with especial readiness with cyanogen and sulphur.

The gold compounds are mostly readily soluble in potassium cyanide, and give rise chiefly to two series of salts, the aurous and the auric cyanides. The former are derived from aurocyanidion, $Au(CN)_2'$, which corresponds to argenticyanidion, and are formed by dissolving aurous compounds in alkali cyanides. The compounds of the second series are the salts of auricyanidion, $Au(CN)_4'$, and are formed from auric compounds and cyanides; they are the better known and the more important of the two classes.

In neither case have the free acids been prepared, but a number of salts are known. These are colourless; they do not exhibit the ordinary reactions of gold, and are, for example, not nearly so readily reduced as these.

The potassium salt, $KAu(CN)_4$, crystallises with $1\frac{1}{2}H_2O$ in colourless, readily soluble plates, and has a technical importance in two different directions. On the one hand, it is used for the electro-gilding of other metals. For this purpose it has the same advantages as are possessed by potassium argenticyanide for silvering (p. 681). As a rule, it is not first prepared specially but potassium cyanide is electrolysed between gold electrodes until a sufficient amount of the substance has been formed in the bath. Its formation takes place at the anode where cyanogen is liberated from the potassium cyanide; the former immediately yields gold cyanide with the gold, which then dissolves in the excess of potassium cyanide with formation of potassium auricyanide. At the same time, hydrogen is liberated and caustic potash is formed at the cathode; the latter must be removed by addition of acid.

Another application depends on the fact that metallic gold dissolves in a dilute solution of potassium cyanide, with co-operation of the atmospheric oxygen, to form potassium auricyanide, according to the equation: $2Au + 8KCN + 2O_2 + 4H_2O = 2KAu(CN)_4 + 6KOH + H_2O_2$. As can be seen from the equation, caustic potash and hydrogen peroxide are formed besides the gold salt. It has already been mentioned that the formation of the peroxide in oxidations by means of free oxygen is a frequent phenomenon (p. 157). The above reaction is made use of on the large scale for the extraction of gold in those cases where it occurs so finely divided that levigation or amalgamation cannot be successfully employed (*vide infra*). South African gold, more especially, is obtained in this way. The gold is again separated by electrolysis from the solutions (for which very dilute potassium cyanide must be employed).

Gold therefore behaves as a base metal towards the solution of potassium cyanide, for it dissolves in it under the joint action of the atmospheric oxygen, in much the same way as copper dissolves in hydrochloric acid under the influence of the air. This is due to its passing into a complex compound in which the concentration of elementary aurion is extremely small. It has already been pointed out that the smaller the concentration of the metal ion in the resulting solution, the more does the metal behave as a base metal towards that reagent (p. 685). This refers not only to the electrical behaviour, for this is only an expression of the chemical properties, but to all chemical processes.

These relations can be interpreted in the following general manner. As has already been frequently emphasised, every possible substance has a tendency to formation, and this is all the greater the smaller its concentration at that point where it could be formed. Of a necessity, therefore, under given conditions, traces of every possible substance must be formed. The noble metals, now, are those for which immeasurably small concentrations of their ions suffice to counteract the tendency to further ion-formation. For this reason gold appears insoluble in the ordinary acids. If, however, the conditions are such that even these minute amounts of ions disappear by being used up in the formation of complex compounds, more gold must pass into solution, and this must continue until the concentration of aurion necessary for equilibrium has been established in the solution. A noble metal, therefore, will appear as base only in those solutions with the components of which it forms complexes, and it will appear all the more base the more stable these complexes are in respect of the metal ion, or the less the amount of metal ion split off by the complex at a given, absolute concentration. This view has been universally confirmed by experience.

We find here the explanation of the solubility of gold in aqua regia, although gold is not (or rather, is only slightly) soluble in nitric acid. The hydrochloroauric acid which is formed is a comparatively stable complex compound in whose solution the concentration of aurion is only very small, while the solution in nitric acid contains more gold and is less stable. Aqua regia, therefore, dissolves gold not because it is a stronger oxidising agent than nitric acid, but because gold is a less noble metal with respect to aqua regia than with respect to nitric acid. It is still less noble towards potassium cyanide solution and free oxygen, which are in themselves no very effective oxidising agents.

Gold also forms complex compounds with substances containing sulphur. The simple thio-acids of gold have already been mentioned; we have still to mention the complex compound which gold forms with the thiosulphates. By the action of a solution of sodium thiosulphate on neutral gold chloride, a salt of the composition $Na_3Au(S_2O_3)_3$ is obtained; it can be precipitated from the solution by the addition of alcohol, has a sweet taste, and does not exhibit the reactions of the ordinary solutions of gold salts. The corresponding aurithiosulphuric acid, $H_3Au(S_2O_3)_3$, can also be prepared by decomposing the barium salt (obtained in a similar manner to the potassium salt).

These compounds play a rôle in the "toning" of positive silver pictures in photography, as they are contained in the combined toning and fixing solutions.

Metallurgy of Gold.—Since by far the largest amount of gold occurs in the metallic state, the metallurgy of gold was for long a mechanical and not a chemical operation. The auriferous sand was treated with running water which carried away the light sand but left the heavy grains of gold behind. If the gold was not contained in sand but in the solid rock (*e.g.* in quartz), this operation had to be preceded by a mechanical disintegration of the rock, unless it was preferred to fuse the whole stone, with suitable additions, whereby the gold, being the densest component, sank to the bottom.

Gold, however, frequently occurs in such a fine state of division that it is carried away in the process of levigation. In these cases it can be extracted with mercury, in which it is readily soluble; the mercury is recovered by distillation.

Still more finely divided gold is extracted with a very dilute solution of potassium cyanide (p. 746).

Metallic gold is not employed in the pure state for coinage and articles of jewellery, as it is too soft, but at most is used in the laboratory for caustic alkali fusions, because it is more resistant to caustic potash and soda in the heat than is platinum or silver. For ordinary usage, gold is alloyed with other metals, generally copper. The amount of gold contained in the alloy for coinage is regulated by Government; English gold coinage contains 91·66 per cent of gold.

Platinum.—Of the six metals of the platinum group mentioned above (p. 742) platinum itself is the most frequent and the most important. Like gold it occurs native and is obtained by levigation. Crude "platinum ore" contains all six metals in varying amounts, and must be subjected to a rather complicated process of separation in order that the components may be obtained in the pure state.

Platinum is a grey-white metal having a density 21·4, and melting at 1770°. It can be welded at a bright red heat, can be drawn to a fine wire, and possesses great resistibility to chemical influences. It is, more especially, not appreciably dissolved by pure acids; its durability under the action of boiling sulphuric acid has already been mentioned (p. 286). It is dissolved by aqua regia, but also rather slowly. It is also fairly stable to electrolytically liberated chlorine. It is attacked, however, in cases where it can combine at a red heat with phosphorus; many a platinum crucible has been eaten through by igniting phosphates along with carbon. Platinum is also attacked by melting caustic potash or soda, while the alkali carbonates can be fused without danger in platinum vessels. On being heated for a long time in contact with carbon, the platinum absorbs some of it, and becomes brittle. It mixes with readily reducible metals, and forms easily fusible alloys; such metals, therefore, must not come into contact with hot platinum vessels. It is indifferent towards hydrofluoric acid.

These properties render platinum of great value both in the laboratory and in the arts; indeed, so much of the metal is used in the latter, that its price has risen to several times its former value.

In the laboratory platinum is used for the most varied purposes, in the form of crucibles, dishes, wire, and foil, especially for exact analysis. In the arts it was formerly chiefly used for concentration retorts in the sulphuric acid manufacture. On account of the change to the anhydride process now taking place in the sulphuric acid manufacture (p. 283), the platinum does not become free, for the new process also requires platinum, although for other purposes. In commercial electrolysis also, electrodes of platinum are often used.

A widely extended application of platinum is due to the fact that its coefficient of expansion is almost the same as that of glass. Platinum wires are, therefore, employed for leading electric conductors air-tight through glass. Whereas, formerly, use was made of this only in scientific apparatus, large quantities of platinum are now used for the conducting junctions in electrical incandescent lamps, the interior of which must be exhausted. Further, much platinum is used in electrotechnics for coating electrical contacts, since the platinum surfaces are not oxidised by the sparks which are there formed, and therefore retain their conductivity.

On account of its high melting point, platinum does not fuse in ordinary flames, not even in the hottest part of the Bunsen flame. It can be readily fused, however, in the oxyhydrogen flame (p. 101), and this is used in the arts on a large scale for the purpose of fusing platinum to a mass; the crucible material is made of burnt lime.

Since most of the platinum compounds decompose at a red heat, leaving a residue of metallic platinum, the latter is in this way obtained as an unfused, finely divided mass, known as *platinum sponge.* In this form platinum exhibits very pronounced catalytic properties, chiefly in the acceleration of numerous gas reactions. Several examples of this have already been given; the most important, technically, is the preparation of sulphur trioxide by means of spongy platinum.

* Spongy platinum was used by Döbereiner, the discoverer of the above property, for the construction of the lamp named after him, which was greatly used at the time of its discovery (1823), when matches did not exist. It depends on the fact that a current of hydrogen gas, when caused to strike on a piece of spongy platinum, unites under its influence so quickly with the atmospheric oxygen that the metal becomes red-hot and ignites the hydrogen. The Döbereiner lamp, therefore, consists of an automatic hydrogen generator (the arrangement of which is seen from Fig. 121), filled with zinc and sulphuric acid, and of a piece of platinum sponge placed in a small box opposite the exit tap. In recent times, the same principle has been employed for the ignition of gas flames by the mere opening of the tap, especially in the case of incandescent burners.

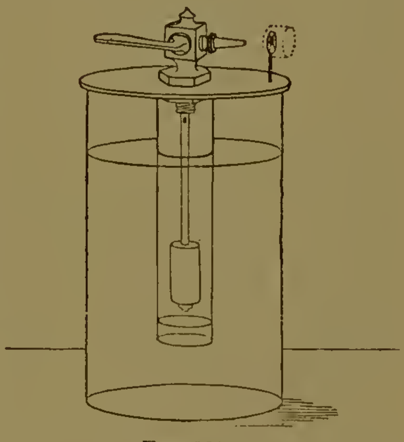
FIG. 121.

Since the catalytic actions of platinum take place at its surface, they are, for a given amount of metal, all the more considerable the greater the surface. This is seen in the very finely divided platinum which is obtained on reducing alkaline platinum solutions with organic substances, *e.g.* formic acid (p. 397.) The metal is then deposited in the form of a very fine powder which, on account of its black colour, is called *platinum black*, and which exhibits the above-mentioned catalytic properties in a high degree. On being heated to redness, it cakes together, and forms grey spongy platinum.

Besides the catalytic actions, platinum black also exhibits absorption phenomena which, by reason of its fine division and correspondingly large surface, are as clearly seen as in the case of charcoal (p. 380). On account of this property it is somewhat difficult to prepare platinum black pure.

Finally, platinum is obtained in the most finely divided state by disintegration by means of an electric arc under water (Bredig). A black-brown coloured colloidal solution is then produced, which exhibits perfectly similar catalytic actions to the other forms, even when present in extremely small amounts. By addition of salts, the platinum is readily precipitated from these solutions, and then exhibits the catalytic actions in a much less degree.

* Apparently connected with these catalytic actions is the property of platinum of dissolving large quantities of different gases, especially hydrogen. Hydrogen diffuses through red-hot platinum with the greatest ease; but, even at the ordinary temperature, platinum, especially in the form of platinum black or spongy platinum, can absorb fairly large quantities of the gas. The hydrogen thereby increases enormously in reactivity, and acts in accordance with its position in the potential series (in the neighbourhood of lead), reducing, for example, more noble metals from their salts, and forming the corresponding compounds, *i.e.* the acid. It must not be supposed that the chemical affinity or the chemical potential of the hydrogen is changed; such an assumption, which is certainly very often made, would be a contradiction of the fundamental laws of the theory of energy. For, if it were the case, one might generate hydrogen without the presence of platinum, and then in the presence of platinum allow it to pass again into the same combination, and would use up less work for the first process than is gained in the second; in other words, any amount of work whatever would be obtained without expenditure, or from nothing. This, however, is shown by experience to be impossible.

* The cause of the changed action of the platinum lies rather in the acceleration of the reactions of hydrogen, and is, therefore, a catalytic action. Gaseous hydrogen reacts so slowly at the ordinary temperature that it appears like an indifferent substance, and from the fact that in the presence of platinum the reaction becomes visible in a short time, while otherwise it would require hours or perhaps years, the view has arisen that there is a change of the chemical potential.

Compounds of Platinum occur in two series, in which the metal acts as divalent or tetravalent. The latter are the better known and the more stable.

Elementary platinion is formed neither in the one nor the other series in any considerable amount; on the contrary, all the more stable compounds of this metal are of a complex character. The variety of these complexes is exceedingly great; only a very few of them can be treated here.

On dissolving platinum in aqua regia, a yellow-red solution is formed which, on evaporation, yields crystals of hydrochloroplatinic acid, H_2PtCl_6. This compound is a strong dibasic acid, which does not contain any considerable amount of chloridion, for it does not give a precipitate of silver chloride with silver salts, but one of silver chloroplatinate, Ag_2PtCl_6. Further, on electrolysing a solution of the acid or one of its salts, it is found that the platinum moves towards the anode and not to the cathode, for the liquid during electrolysis in the neighbourhood of the cathode becomes poorer, and in the neighbourhood of the anode richer in platinum,[1] which shows that the platinum is not present as a cation.

Of the salts of hydrochloroplatinic acid, we have already met with the difficultly soluble potassium salt (p. 442), since it is used for the separation and analytical determination of potassium. It is a salt which crystallises in anhydrous, regular octahedra, and is much more readily soluble in hot than in cold water. By addition of alcohol it is almost entirely precipitated from its aqueous solution.

Sodium platinochloride is readily soluble in water, and crystallises with $6H_2O$. Ammonium platinochloride resembles the potassium compound in being difficultly soluble; it is used for the separation of platinum from the solutions of the crude platinum ores. On being heated it readily decomposes into ammonium chloride and chlorine, which escape, and metallic platinum, which remains behind in the form of spongy platinum (p. 749).

By carefully heating hydrochloroplatinic acid in a current of chlorine, platinum tetrachloride, $PtCl_4$, is obtained as a crystalline mass similar to hydrochloroplatinic acid, but not deliquescent. It readily dissolves in water; the solution contains, like that of gold chloride, an oxy-acid, H_2PtCl_4O, which is formed by the absorption of the elements of water. The very dilute solutions have the remarkable property that their conductivity very rapidly increases when they are illuminated,—a behaviour which is probably connected with a hydrolysis with splitting off of hydrochloric acid.

On adding excess of sodium carbonate to a solution of hydrochloroplatinic acid, concentrating and extracting the residue with acetic acid, platinic hydroxide, $Pt(OH)_4$, is obtained as a red-brown powder, which is soluble in strong acids (but not in weak acids like acetic acid) and in alkalis. The solutions in acids contain platinic salts, which are greatly dissociated hydrolytically, but presumably also contain a little tetraplatinion ($Pt^{\cdot\cdot\cdot\cdot}$); they are of a yellow-brown colour. The alkaline solutions contain platinates, *i.e.* salts of the acid H_2PtO_3, some of which have been prepared in the solid state.

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[1] At the electrodes themselves the reaction is apparently the opposite, metallic platinum separating out on the cathode. This is, however, a secondary reaction due to the fact that the hydrogen, which is conducted by the current to the cathode, is not discharged there, but reduces the platinum solution present, and the metal is deposited.

From the solutions of the platinum compounds, sulphuretted hydrogen slowly precipitates black platinum sulphide, which dissolves in excess of alkali sulphides to a dark-brown solution, with formation of a thioplatinic acid.

From the compounds of platinichloridion, compounds of platinochloridion $PtCl_4''$ are formed by means of reducing agents. Thus, on warming an aqueous paste of potassium platinichloride with cuprous chloride, a dark solution is obtained from which dark-red crystals of the soluble salt K_2PtCl_4 separate out. The free acid is known only in solution; the anion $PtCl_4''$ is ruby-red in colour. The potassium salt is employed in photography for the production of platinotypes, which consist of metallic platinum. For this purpose it is spread on paper, along with ferric oxalate, and exposed to light; in the light the ferric salt is reduced to ferrous salt (p. 582). If the paper is then passed through a solution of potassium oxalate, a reduction of the platinum occurs at those parts at which the action of light had occurred, and a positive is obtained in a grey-black colour which, in accordance with the stability of metallic platinum, is very resistant to air and light. With a very weak acid solution of potassium platinochloride, also, silver prints can be converted into platinum ones, *i.e.* one can "tone" with platinum.

From the solutions of the platinochlorides, alkalis precipitate black platinous hydroxide, which has no acid properties.

Platinous chloride, $PtCl_2$, is obtained by heating hydrochloroplatinic acid to 250°-300°, or by heating spongy platinum to the same temperature in a current of chlorine. It is a green-brown powder, which does not dissolve in water, but is readily soluble in hydrochloric acid; with the latter it forms a hydrochloroplatinous acid.

On passing carbon monoxide over platinous chloride, very remarkable compounds are formed which contain the components in the proportions 1 : 1, 1 : 2, and 1 : 3. The first volatilises without decomposition at about 250°, and thus stands in conspicuous contrast to all other platinum compounds, which are not volatile, but decompose in the heat. They are yellow or yellow-red crystalline substances.

On allowing a solution of potassium platinochloride to stand with potassium nitrite in a warm place, potassium platinonitrite, $K_2Pt(NO_2)_4$, soon crystallises out in colourless, difficultly soluble crystals. The free acid, $H_2Pt(NO_2)_4$, has also been prepared. The salts readily take up two combining weights of halogen.

Of the numerous other series of complex compounds which platinum forms, we may still mention the ammonia and the cyanogen compounds. The ammonia compounds belong to two series, corresponding to the platinous and platinic compounds. Their empirical composition is that of divalent or tetravalent salts of platinum combined with one to four combining weights of ammonia, NH_3, often along with water. Moreover, they exhibit specific properties, showing that they are salts of new cations in which neither the ammonia nor the platinum gives its usual reactions. These compounds are very similar to the corresponding compounds of cobalt (p. 613), more especially also in the fact that the halogens and acid residues present are only partially separated as ions, and in part form constituents of the cations. The hydroxides of several of these have been prepared, and are soluble substances with a strongly alkaline reaction. For the theory of these compounds, cf. p. 614.

The complex compounds with *cyanogen* are derived from the divalent cyanoplatinosion, $Pt(CN)_4''$. The potassium salt is formed by dissolving platinous chloride in a solution of potassium cyanide, and also by melting potassium cyanide with spongy platinum; it is a bright yellow salt exhibiting a blue iridescence. The barium compound is formed by mixing platinous chloride and barium carbonate with water, and passing hydrocyanic acid into the hot liquid. It is a bright yellow salt exhibiting violet-blue iridescence. The magnesium salt, which can be prepared in the same way, is crimson red with green metallic lustre, the property of surface iridescence, dependent on the crystalline form, being possessed by all the salts of this series. The barium compound also exhibits in a very marked manner the phenomenon of fluorescence, and it converts, not only the ordinary ultra-violet, but also the Röntgen and uranium rays (p. 735) into visible light, and its application is in accordance with this property.

From the solution of the barium salt, the free hydrocyanoplatinous acid is obtained by means of dilute sulphuric acid; it is colourless in solution, but in the solid state it exhibits a variety of lustrous colours, according to the amount of water it contains.

The salts of this series readily take up two combining weights of halogen, but these are only feebly united; the corresponding compounds likewise generally crystallise well.

Palladium.—Palladium was discovered by Wollaston in 1803 in platinum ore. It is the least noble of the platinum metals, as it readily dissolves in nitric acid. It resembles platinum in its combining relations, for it forms divalent and tetravalent compounds; in this case, however, the divalent compounds are the more stable.

Metallic palladium has a density of 11·8, and melts at 1500°. It is a metal similar to platinum, and has the special property of uniting with large amounts of hydrogen to form a compound of metallic appearance, the nature of which has not yet been sufficiently explained.

The combination of the two substances takes place most rapidly at 100°, and is all the more rapid the more finely the metal is divided. With finely divided metal, 800 volumes of hydrogen are absorbed by one volume of the metal. Still more hydrogen is absorbed on employing the metal as cathode in dilute sulphuric acid; the amount of gas then absorbed increases with the strength of the current; a portion of the hydrogen so absorbed, however, escapes immediately the current is stopped, while another portion is in stable combination. If the temperature is raised, the palladium hydride again decomposes into its components; it does not, however, follow the ordinary law of dissociation, according to which the pressure is independent of the degree of decomposition; in this case there is a dependence.

The hydrogen absorbed by palladium has a strongly reducing action, and it has therefore often been regarded as existing in a special condition. In this case, however, as in the case of platinum, we are dealing only with a catalytic acceleration of the reaction.

* If galvanic cells are constructed containing hydrogen along with various metals, such as gold, platinum, or palladium, no electromotive force is observed if the hydrogen is always present in excess. This is a proof that the chemical potential of the hydrogen is not increased by the palladium.

Of the chemical compounds of palladium, palladious nitrate, $Pd(NO_3)_2$, may be mentioned, which is formed by dissolving the metal in nitric acid. It is a very deliquescent salt, the solution of which is dark brown in colour; this colour may be ascribed to dipalladion, $Pd^{\cdot\cdot}$. On adding alkali carbonates to these solutions, carbon dioxide is evolved, and a dark brown precipitate of palladious hydroxide, which on ignition decomposes only with difficulty into metal and oxygen, is deposited. Dipalladion unites with iodidion to form a dark-brown compound, which is soluble with extreme difficulty in water. Since bromidion and chloridion do not give such a precipitate, palladious nitrate can be used as a reagent for iodidion.

If palladium is dissolved in a large excess of aqua regia, a solution of hydrochloropalladic acid, H_2PdCl_6, is formed, from which the potassium salt can be obtained as a difficultly soluble crystalline powder consisting of scarlet octahedra. Even on heating the acid solution to boiling, chlorine escapes and hydrochloropalladious acid, H_2PdCl_4, is formed, the potassium salt of which is very similar to the corresponding platinous compound (p. 752).

On evaporating a solution of palladium in aqua regia to dryness, hydrogen chloride and chlorine escape, and palladious chloride, $PdCl_2$, is obtained, which dissolves in water with a red-brown colour.

The combining weight of palladium is Pd = 106.

Iridium.—On treating platinum ore with aqua regia, part of the iridium is dissolved along with the platinum, and part remains alloyed with osmium as osmiridium, which is not attacked by aqua regia. The dissolved portion is precipitated along with the platinum by means of ammonium chloride, and its presence is recognised even in comparatively small amounts by the fact that the compound of platinum chloride and ammonium chloride has a yellow-red or red-brown colour instead of bright yellow. This portion of iridium is often left in the platinum used in the arts, since the metal thereby becomes harder and more resistant to chemical influences.

Pure iridium scarcely melts even in the oxyhydrogen flame, and can be worked only with difficulty. It has the density 22, the hardness of slightly tempered steel, and is only slowly attacked even by aqua regia; it is more readily attacked when it is in a state of fine division. On gently heating a mixture of the metal and common salt in a current of moist chlorine, the former can be converted into the sodium salt of divalent chloroiridanion.

Iridium forms three series of compounds in which it is di-, tri-, and tetravalent. The divalent compounds are the least stable and are little known; the other two series pass very readily one into the other, so that it is hardly possible to say which is the more stable. In both series the typical compounds are the complex chloroiridium ions—the trivalent chloroiridosion, $IrCl_6'''$, and the divalent chloroiridanion, $IrCl_6''$. The former anion is green-brown, the latter dark-red. The change of colour accompanying the ready conversion of the two series into one another, gave rise to the name of the element (from *iris*, a rainbow).

Potassium chloroiridate, K_2IrCl_6, resembles potassium chloroplatinate in its solubility relations; it crystallises in small dark-red octahedra, and is obtained by heating a mixture of finely divided iridium and potassium chloride in a current of moist chlorine to a gentle red heat. The corresponding sodium salt crystallises like the platinum compound with $6H_2O$, and is readily soluble. By reduction with sulphurous acid in acid (or with alcohol in basic) solution, chlorine and sodium chloride are split off, and sodium chloroiridite, $Na_3IrCl_6 . 12H_2O$, which is a very soluble salt, is obtained. The potassium salt obtained in a similar manner from the chloroiridate, is also readily soluble. Both are readily reconverted by oxidising agents into the higher series.

With ammonia iridium forms numerous complex bases, which are similar to those of platinum.

The combining weight of iridium is Ir = 193·0.

Rhodium.—Rhodium stands to iridium in a relation similar to that of palladium to platinum. Like iridium it forms three series of compounds; in contrast with iridium, however, the highest series is here the least stable. This depression of the region of stability towards the lower type, is present also in the case of palladium compared with platinum, and occurs in both cases in the element of lower combining weight.

Rhodium occurs in comparatively small quantity in platinum ores. It was discovered in 1803 by Wollaston, and has obtained its name from the rose-red colour of its salts.

Metallic rhodium is less refractory than iridium, but more so than platinum. In the pure state it is ductile and has the density 12. The finely divided metal has very pronounced catalytic properties; for example, it decomposes formic acid in aqueous solution into hydrogen and carbon dioxide: $H_2CO_2 = H_2 + CO_2$, *i.e.* it so greatly accelerates this reaction, which takes place of itself in very small amount, that the gases escape with effervescence. Other organic compounds are also changed in a similar manner; this is a proof that very many of these substances are unstable compounds, and gain an appearance of stability only from the slowness of their spontaneous decomposition.

The best known compounds of rhodium are those of the trivalent type; from these, apparently, two different chlororhodium ions, viz., $RhCl_7''''$ and $RhCl_6'''$, appear to be derived; salts, at least, of these two types are known. The alkali salts are soluble with a red colour in water.

A fairly large number of complex ammonia compounds are also known in the case of rhodium.

The combining weight is Rh = 103·0.

Osmium and **Ruthenium** are distinguished in a very characteristic manner from the other four platinum metals by their property of forming readily volatile oxygen compounds; these are produced, although slowly, by heating the metals in the air, and volatilise with the steam in the treatment of the crude platinum ore with aqua regia. These compounds contain four combining weights of oxygen to one of the metal, and behave as almost indifferent substances; at all events, the acid properties of the hydroxides (unknown in the free state) are only feebly developed.

Osmium has the density 22·5 in the crystalline state and is the densest of all known substances. It is almost infusible, is very hard, is insoluble in aqua regia, but passes slowly into the volatile tetroxide on heating in oxygen. By fusion with zinc and treatment of the alloy with hydrochloric acid, it is obtained in a finely divided state as a black powder, which, on being heated in the air, smoulders and forms the tetroxide; from tin, however, it is obtained in crystals with a metallic lustre.

Osmiridium, which remains after treating the platinum ore, forms hard, silver-white laminæ, and is used for tipping gold pen-nibs, which do not wear down with use. On being heated with common salt in a current of wet chlorine (*vide supra*) the osmium volatilises in the form of the tetroxide.

Osmium tetroxide is a white, readily fusible crystalline mass which slowly dissolves in water and readily volatilises with steam. It has a strong, very unpleasant smell, recalling that of chlorine, and a highly poisonous action, because it is reduced by the tissues to metallic osmium, which is deposited and exercises a continual irritation; the eyes, more especially, are powerfully attacked. The solutions exhibit oxidising actions but no acid reaction; if an alkali is added, the greater portion of the tetroxide can then be distilled off, showing that the corresponding salt undergoes hydrolysis to a large extent, and is therefore formed only in very small amount.

Aqueous solutions of osmium tetroxide are used in histology for hardening animal tissues.

On careful reduction, the alkaline solutions of osmium tetroxide are converted into the salts of osmanion, OsO_4'', the acid not being known either in the free state or as the anhydride. That a new anion has been formed is evidenced by the fact that the liquid, which was previously colourless, becomes red-violet; on addition of acids, however, the osmic acid decomposes into tetroxide, which volatilises, and the hydroxide of tetravalent osmium, which is deposited as a black precipitate, if any oxyacid has been used; in hydrochloric acid, however, the latter is soluble.

With chlorine, osmium forms two chlorosmium ions, $OsCl_6'''$ and $OsCl_6''$. The former anion is cherry red, the latter golden yellow. The salts of the second series are formed by treating osmium and alkali chlorides with moist chlorine, those of the first are obtained by the reduction of the latter, and are unstable.

Finally, osmium compounds of a divalent type have been obtained by the reduction of the higher compounds. The corresponding salts, in which the osmium is present as a divalent cation, are dark-blue in colour; they oxidise very readily to a higher stage.

The combining weight is $Os = 191$.

Ruthenium was discovered by Claus in 1845. It is a grey metal of density 11, which fuses only with difficulty but more readily than osmium. It is fairly resistant to aqua regia; on fusion with caustic potash and saltpetre it is attacked with formation of potassium ruthenate.

On distilling the solution produced while a current of chlorine is at the same time passed through it, ruthenium tetroxide passes over as a yellow crystalline mass, which melts as low as 26°, and boils about 100°; at this temperature, however, explosions readily occur. It seems to be formed also in minute traces on heating the metal in the air. The vapour is yellow, and the molar weight corresponds to the formula RuO_4. It dissolves in water forming a yellow liquid, which is unstable.

From the oxide, two series of salts are formed with bases, with loss of oxygen, viz., the dark green perruthenates, $MRuO_4$, and the orange-red ruthenates, M_2RuO_4; between these two, therefore, the same relation exists as between the permanganates and the manganates, and their reciprocal transformation also takes place under perfectly similar conditions, the latter being more stable in alkaline liquids, the former in acid or neutral.

With chlorine, ruthenium forms compounds of the di-, tri-, and tetravalent type; the last two form hydrochlororuthenium acids, H_2RuCl_5 and H_2RuCl_6; the former are yellow, the latter red.

The combining weight of ruthenium is Ru = 101·7.

CHAPTER XLIV

THE CHOICE OF COMBINING WEIGHTS AND THE PERIODIC SYSTEM

General.—In the preceding chapters the question as to which of the possible multiples of the combining weight of each element is the most suitable has not been discussed, and we now proceed to examine whether a general answer can be given to the question at all.

As the most obvious rules for the choice of the combining weights, the two following will evidently be laid down, viz. the formulæ shall, in the first place, be as simple as possible, and, in the second place, similar compounds shall have similar formulæ. These two rules lead, in many cases, to concordant results, in other cases, however, to contradictory ones.

Thus, according to the *principle of simplicity*, the combining weight of those elements which form only one compound with oxygen will be chosen, so that the compound contains *one* combining weight of each element. This is, for instance, the case with zinc and cadmium, whose oxides are written ZnO and CdO. In the second place, in accordance with the *principle of similarity*, of the two oxygen compounds of copper, cupric oxide must be formulated in agreement with zinc oxide, because these two exhibit various points of similarity in their compounds. Hence, it follows, that cuprous oxide must be written Cu_2O.

If now, we are dealing with silver oxide, we should, in accordance with the principle of simplicity, write the formula AgO, and make $Ag = 215{\cdot}8$. This, however, would be in conflict with the second principle, for the silver compounds are very similar to the cuprous compounds. We have the choice, therefore, of violating the one or other principle; they cannot both be followed at the same time.

Similar holds in the case of iron and aluminium. On account of its similarity to zinc oxide and cupric oxide, ferrous oxide must be written FeO; from this, the formula Fe_2O_3 would follow for ferric oxide. Aluminium forms only one oxygen compound and would, therefore, in accordance with the principle of simplicity, have to be written AlO, Al being made equal to 40·5. In this way, however, attention is not paid to the undoubtedly very great similarity to ferric oxide, and in order to give expression to this, we must write Al_2O_3, and thus violate the principle of simplicity.

To give effect to both of the above principles at one and the same time, is not possible without producing contradictions, and one has often to decide which of the two principles, one will violate. In general, the principle of similarity has the preference.

Isomorphism.—It is, however, not easy in any given case to decide as to the degree of similarity to be taken into account. Silver oxide and lead oxide also show a considerable amount of similarity in their general relations, more especially in respect of the solubility of their salts, and yet the two are differently formulated, viz. Ag_2O and PbO. In order to arrive at definite rules, we must give up the general "similarity" and choose some demonstrable property as basis. In *isomorphism* (p. 308) we obtain such a property. We shall therefore lay down the principle: The combining weights shall be chosen such that isomorphous substances have similar formulæ. As a matter of fact, this principle can be followed without obtaining contradictions, and all isomorphous pairs and groups mentioned in this book have received concordant formulæ.

A complete system of combining weights, however, cannot be obtained in this way, since the isomorphous groups are mostly restricted to a small number of compounds, and the relations existing between elements belonging to different groups (*e.g.* manganese) are not sufficient to unite all the groups. Further aids must therefore be looked for.

The Molar Weight.—Such an aid is afforded by the conception of molar or molecular weight, if we lay down the condition that all formulæ corresponding to a molar weight shall contain only a whole number of combining weights of the elements (p. 88). The molar weight is a number which can be deduced from the gaseous density or from the depression of the freezing point or elevation of the boiling point (p. 155), and which can be determined independently of doubtful suppositions, and purely by experiment. The question whether the above condition is fulfilled can therefore be tested in the case of all substances which can be observed in the gaseous state or of which solutions can be prepared. As a matter of fact, various doubtful cases have been decided by this means. Thus, for example, beryllium was regarded by many investigators as an earth metal, and its chloride was, in analogy to that of aluminium, written $BeCl_3$, *i.e.* there was taken as the combining weight of beryllium that weight which was combined with 3 × 35·46 parts of chlorine, viz. 13·5. When, however, one succeeded in determining the vapour density of beryllium chloride its molar weight was found to be 80. From this it follows that only *two* combining weights of chlorine can be contained in beryllium chloride. The combining weight of the element must therefore be taken as 9, and the chloride be written $BeCl_2$.

These considerations, of course, lead much further than those of isomorphism alone, but even they are not perfectly decisive. It is, indeed, conceivable, although generally not very probable, that besides the compounds whose molar weights are known, other compounds of a particular element exist, the molar weight of which contains only a fraction of the combining weight deduced from the former compound. This would not necessitate a contradiction to the other compounds, but would merely lead to the assumption of several combining weights in the former compounds. In other words, from the molar weights there can be deduced only the limit above which the combining weight does not lie, but it cannot be proved that the combining weight is not a fraction of that hitherto chosen.

The Atomic Heat.—A law discovered in 1818 by Dulong and Petit, and which has since then been confirmed in many other cases, admits of no such doubt. This states that the thermal capacity of the elements referred to one combining weight, or the *atomic heat*, is constant and equal to about 6 calories or 25 *kj* for each degree.

By the term thermal capacity of a body there is understood the ratio between the amount of heat communicated to the body and the elevation of temperature which the latter experiences. If, therefore, the heat Q is introduced into the body, the temperature of which thereby rises t°, the thermal capacity of the body is $k = Q/t$. This quantity k is evidently inversely proportional to the weight of the body investigated, for the elevation of temperature will be smaller in the same proportion as the amount of substance increases to which the same quantity of heat is communicated. It has, however, also been found that equal weights of different substances experience very different elevation of temperature with the same amount of heat; that is, in other words, the specific heat of different substances is different, for the term *specific heat* has been applied to the thermal capacity referred to the unit of weight. If, however, we do not consider equal weights, but weights which are in the ratio of the combining weights, *these quantities of substance have the same thermal capacity* when we are dealing with the elements in the solid state. Calling the thermal capacity referred to the combining or atomic weight, by the name *atomic heat*, the law states that the atomic heats of the solid elements are equal.

This law is not universally valid. In the first place, as above-mentioned, it is valid only for the solid state; liquid, and especially gaseous elements, are not subject to it. Further, it is valid not for all solid elements, but only for those whose combining weight is not less than 30. The elements which are below this limit have, in the sense of the law, too small an atomic heat.

Result.—If we now ask how these different principles for the choice of the combining weight can be united, in so far as they affect the same elements, we find that they agree well with one another. A system of combining weights can be drawn up which allows of the expression of all isomorphism relations by concordant formulæ, and of all molar weights by integral values of the combining weights, and whereby also the atomic heats of the solid elements (with combining weight above 30) are expressed by approximately the same numbers. These are the combining weights of which use has continually been made in this book, and which are at the present day universally accepted by the chemists of all countries. Nowhere in this work has it been necessary to write formulæ representing actually determined molar weights with fractions[1] of the combining weights. Further, in all cases of isomorphism, the formulæ of isomorphic compounds are similar, and that the rule of Dulong and Petit is fulfilled is seen from the following table:—

	kj.		kj.
Lithium	28	Molybdenum	29
Beryllium	16	Ruthenium	26
Boron	18 to 17	Rhodium	25
Carbon	3 to 23	Palladium	27
Sodium	28	Silver	26
Magnesium	26	Cadmium	26
Aluminium	24	Indium	27
Silicon	16 to 24	Tin	27
Phosphorus	23	Antimony	26
Sulphur	24	Tellurium	25
Potassium	27	Iodine	28
Calcium	28	Lanthanum	26
Chromium	26	Tungsten	26
Manganese	28	Iridium	26
Iron	26	Platinum	26
Cobalt	26	Gold	26
Nickel	27	Osmium	26
Copper	25	Mercury	27
Zinc	26	Thallium	28
Gallium	23	Lead	27
Arsenic	26	Bismuth	26
Selenium	25	Thorium	27
Zirconium	25	Uranium	28

The Periodic System.—Attention has been repeatedly drawn to the existence of regularities between the combining weights of similar elements, which generally assumed the form that the differences in the numerical values of corresponding elements in different groups are approximately equal. The question here arises whether we are dealing with any fairly general regularity, and if so how this is to be expressed.

The answer has been sought for in very different ways. As usual, the simplest has been arrived at last. If the elements are arranged in a series simply according to the numerical values of the combining weights without regard to any other circumstance, the following is the result.

---

[1] In some few cases fractions have been written in the statement of the water of crystallisation of salts. Since, at present, molar weights can be determined only for gases or vapours and for dissolved substances, but not for solid substances, no contradiction exists.

In this series similar elements always occur at regular intervals. If then the series is divided into a number of sections, so that each section commences with a member of a definite family, it is found that the second, third, and following positions of the sections are also filled by elements corresponding to one another.

The table on p. 764 has arisen by dividing the series of the elements, as determined by the values of the combining weights, into such sections; these sections have then been placed one below the other. In this way perpendicular columns are obtained in which similar or related elements stand under one another.

The different rows have also been alternately shifted somewhat relatively to one another. As can be seen, the mutual relation between those elements which are most closely allied to one another thereby receives better expression.

Thus, in the column headed 0, we find all the elements of the argon type, which are distinguished by their inability to form chemical compounds. Under I. there are, on the one hand, the monovalent alkali metals, on the other hand the monovalent heavy metals, copper, silver, gold.

Under II. there stand the divalent alkaline earth metals, and along with them, the heavy metals of the zinc group.

Under III. are the earth metals along with the corresponding heavy metals gallium and indium.

Under IV. the tetravalent elements are found. The first representatives of these have no longer a metallic character, just as the first non-metal appeared in the preceding group in the case of boron; the metals of the titanium group on the one hand, and of the tin group on the other, then follow.

Column V. also contains, to begin with, non-metals which can act as trivalent or as pentavalent; in the lower portion there are the corresponding tri- and pentavalent metals.

In column VI. are di- and hexavalent elements; the non-metallic character can be followed further down the column.

Column VII. contains the typical non-metals, the halogens, which can act, on the one hand, as monovalent, on the other hand, as heptavalent.

Finally, the last column contains the two families of the iron metals and the platinum metals, which do not quite fall into line with the rest of the system.

In all these columns the general rule can be observed that the basic properties (*i.e.* the tendency to form cations) increases with increasing combining weight; the power of forming anions, however, decreases.

As can be seen, the table is not complete, but contains many positions unfilled. It cannot be otherwise, for there is no justification for the assumption that all existing elements have already been dis-

PERIODIC ARRANGEMENT OF THE ELEMENTS

0.	I.	II.	III.	IV.	V.	VI.	VII.	
He, 4	Li, 7	Be, 9·1	B, 11	C, 12	N, 14	O, 16	F, 19	...
Ne, 20	Na, 23	Mg, 24·4	Al, 27·1	Si, 28·4	P, 31·0	S, 32·1	Cl, 35·5	...
A, 40	K, 39·1	Ca, 40	Sc, 44·1	Ti, 48·1	V, 51·2	Cr, 52·1	Mn, 55·0	Fe, 56 Ni, 58·7 Co, 59
Kr, 82	Cu, 63·6	Zn, 65·4	Ga, 70	Ge, 72	As, 75	Se, 79·1	Br, 80·0	...
X, 128	Rb, 85·4	Sr, 87·6	Y, 89	Zr 90·6	Nb, 94	Mo, 96·0	...	Ru, 102 Rh, 103 Pd, 106
...	Ag, 107·9	Cd, 112	In, 114	Sn, 118·5	Sb, 120	Te, 127	I, 126·9	...
...	Cs, 133	Ba, 137·4	La, 138, etc.	...	...	...	...	...
...	...	...	...	...	...	...	...	...
...	...	...	Yb, 173	...	Ta, 183	W, 184	...	Os, 191 Ir, 193 Pt, 195
...	Au, 197·2	Hg, 200·3	Tl, 204·1	Pb, 206·9	Bi, 208	...	...	...
...	...	...	...	Th, 232	...	U, 240	...	...

covered and investigated. It is, however, worthy of notice that up to the combining weight 140, scarcely an element is wanting. At this point there is a large blank, and only between 170 and 240 is there again some degree of completeness. At the time, about 1860, when the regularities above described were discovered by Newlands, L. Meyer, and Mendeléef, many more of the elements were wanting, and it was possible, according to the law of similarity, to predict with very fair approximation, the properties of those elements whose places were empty. In this way Mendeléef, especially, predicted the properties of several elements unknown at that time, and the discoveries which were subsequently made amply confirmed most of these predictions.

Besides the general relations of chemical combination, the arrangement of the elements according to the magnitude of their combining weights affords a fairly complete systematisation of the physical properties, both of the free elements and of their corresponding compounds. Thus, on passing continuously along the horizontal rows, we pass through a regular transition from the region of the metals to that of the non-metals, to again commence with metals at the beginning of a new row.

The whole series, then, falls into a number of periods, and the whole system has therefore received the name *periodic law.* The periodic character is seen most clearly by graphically representing definite properties of the elements. Such a representation is given in Fig. 122 of two properties, the atomic volume[1] and the melting point.

Most of the properties of the elements, so far as they can be measured, yield similar figures, so that it has been stated generally: *The properties of the elements are periodic functions of their combining weights.*

The same relations are seen also in the case of comparable compounds, *e.g.* the oxides, chlorides, sulphides, etc., in respect of their different properties. Compare, for example, the solubility relations of the chlorides of the elements and their behaviour generally with water, in the light of the table.

The form of the above regularities, finally, leads to the view that the values of the combining weights themselves must stand in a regular relation to one another. The first idea is that the members are characterised by constant differences of their combining weights. We can at once satisfy ourselves, however, that only a very rough approximation to such a relation exists. Thus, for example, the differences between the corresponding elements of the first and second horizontal series amount to, 16, 16, 15·3, 16·1, 16·4, 17·0, 16·1, 16·5, and is therefore fairly constant although the deviations are far above

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[1] By atomic volume is meant the product of the extensity and the combining weight. In accordance with the definition of extensity (p. 27), it represents the volume in cc. occupied by the combining weight in grams of the particular element.

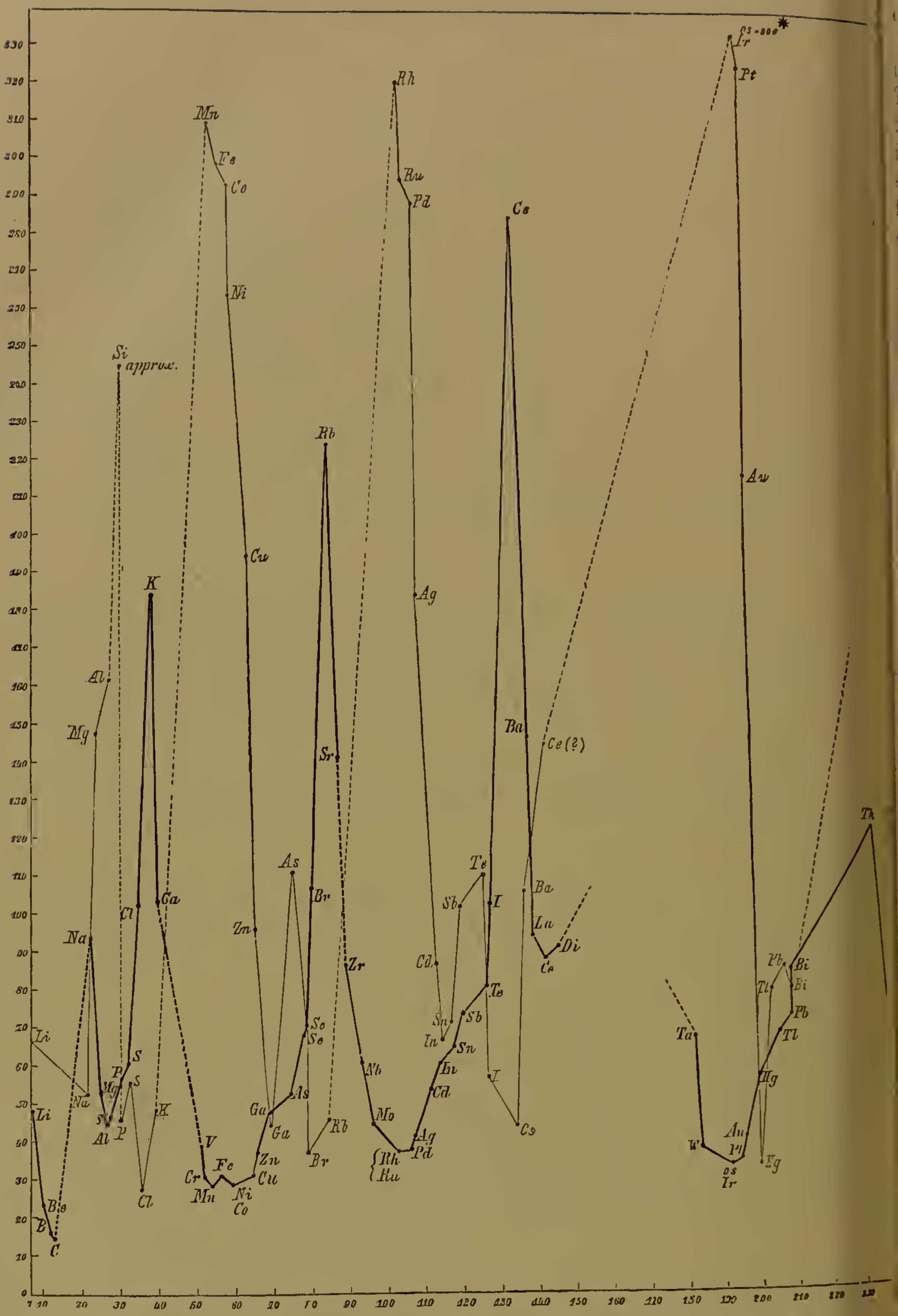

FIG. 122.—The dark line gives the atomic volumes, the light one, melting points in absolute temperature. T ordinates of the atomic volumes are multiplied by 4, those of the melting points are divided by 7. The p marked * lies 66 divisions higher.

the possible errors in the determination of the combining weights. The third and fourth rows, however, give the differences 25, 24·5, 25·4, 27·9, 23·9, 23·8, 27·0, 25·0, and these exhibit much larger and irregular variations. A complete table of the existing differences shows that no apparent regularity is present, and there remains therefore in these numbers an element of chance, *i.e.* of the unknown, which one has not yet succeeded in overcoming.

With this there is connected the fact that in the two cases argon-potassium and tellurium-iodine, the principle of strict sequence according to the magnitude of the combining weight, must be violated, in order not to come into conflict with facts; for in both cases, the larger and not the smaller of two neighbouring combining weights comes first. In both cases the general position of the elements is so undoubted that there has never been any uncertainty as to where they should be placed in the table; the hope, however, that a more exact determination of the combining weights would establish the expected order of sequence, has not been fulfilled.

It is also not to be denied that several arrangements occur in the table which do not correspond very well to the chemical relations. Thus, copper and mercury, which have a very great chemical similarity, occur in different columns; likewise, barium and lead, thallium and silver. Other points might also be cited in which the arrangement given by the periodic system is by no means the most natural.

To the question, then, as to what position should be adopted with regard to these and similar imperfections of the periodic system, we would say, that we are here not dealing with a law of nature in the strict sense, but with a principle of classification of not very exactly defined things. What we call the chemical character of an element and employ for the estimation of its similarities and differences with respect to other elements, is made up of the sum total of the chemical processes and physical properties known to us which this element and its compounds exhibit. It must, however, be at once admitted that our knowledge of these processes and properties is incomplete and highly one-sided. It is incomplete even by reason of the limitation of all human knowledge; it is one-sided in the highest degree because of all possible chemical processes, those occurring at medium and slightly higher temperatures are known with incomparably greater thoroughness than, for example, the processes occurring at much higher temperatures. A further and very great degree of one-sidedness consists in the preference given to the chemical processes taking place in aqueous solution, which the special properties of the large class of saline compounds has urged upon us. Their *technical* and *physiological* importance is certainly much greater than that of the other processes, but for purposes of systematisation they ought not to receive the preference if we would take *all* properties into consideration. To employ a picture, we know only a certain, and, in part, somewhat arbitrarily cut section of the great organism of chemical facts, while the rest of the body remains almost a secret to us. We must not therefore be surprised if in this chance section we cannot gain a view of the laws ruling the whole organism.

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